TRANSACTIONS
American Society for Steel Treating
VOL. XXI JANUARY-DECEMBER 1933

CREEP CHARACTERISTICS OF METALS AT ELEVATED TEMPERATURES

By A. E. White and C. L. Clark

Abstract

This paper discusses creep testing from some of its fundamental aspects. It begins by giving a brief historical development of physical testing, leading up to creep tests. Because of space limitations it only describes the creep testing equipment in use at the University of Michigan. It develops quite fully the methods employed in the plotting of data, pointing out the importance of selecting suitable ordinates. It shows the differences due to the single step, up-step, and down-step methods of loading.

The paper discusses in some detail the influence of grain size, chemical composition, methods of manufacture, heat treatment and rate of creep.

PREVIOUS to 1920 the physical testing of metals was conducted almost exclusively at atmospheric temperatures. The tensile properties were the ones most commonly reported. They were obtained by determining the elastic limit, the yield point, the ultimate tensile strength, the per cent elongation, and the per cent reduction of area. In refined testing the relationship of stress to strain is determined for values up to the elastic limit. Plotting data thus obtained gives stress-strain diagrams such as shown in Fig. 1. The International Congress for Testing of Materials in 1906 defined the elastic limit as the stress per unit area sufficient to cause a permanent set of 0.2 per cent and the proportional limit as the stress which produced

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, who are members of the society, A. E. White is director, department of engineering research, University of Michigan, Ann Arbor, Michigan, and C. L. Clark is associated with him in this department. Manuscript received April 30, 1932.

a permanent deformation of 0.001 per cent. Most of the data were obtained with testing equipment accurate only to about one-thousandth or one ten-thousandth of an inch. In fact, greater accuracy was not sought for.

At that time iron and steel were seldom used at temperatures in excess of 750 degrees Fahr. (400 degrees Cent.). It happens that some steels exhibit their maximum strength at this temperature. The properties of steel at room temperature were, therefore, sufficiently accurate for designing equipment to be used up to 750 degrees Fahr.

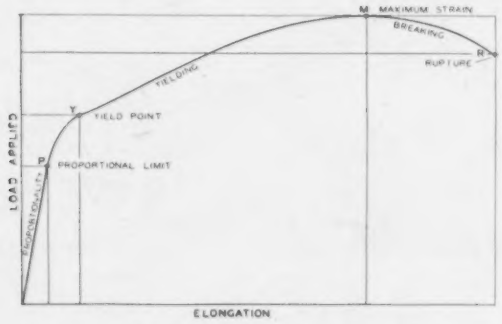


Fig. 1—Stress-Deformation Diagram of a Tension Test.

(400 degrees Cent.). Since 1920 technical development has created a demand for metals which will operate satisfactorily at temperatures ranging from 750 to 1300 degrees Fahr. (400 to 705 degrees Cent.) and in some cases to even higher temperatures.

Testing at elevated temperatures was at first conducted to determine what are termed short-time tensile properties. Experience has shown, however, that often even the short-time proportional limit modified with a conservative factor of safety is of inadequate accuracy to be used for purposes of design. This is due to a property called creep which is the tendency for continuous flow or deformation under stress. It has been found that at room temperature copper, brass, aluminum, and aluminum alloys will break in tension under loads which were 10 to 20 per cent below the commonly accepted elastic limits if sufficient time were permitted. The time under these conditions will vary from 25 days to 9 months. At elevated temperatures creep becomes a very important consideration in design because not only is it necessary to have a material which will not rupture in service but also it is essential that it will not stretch or deform when in use over long periods of time. These needs have resulted in a new technique of testing. The creep test is most fre-

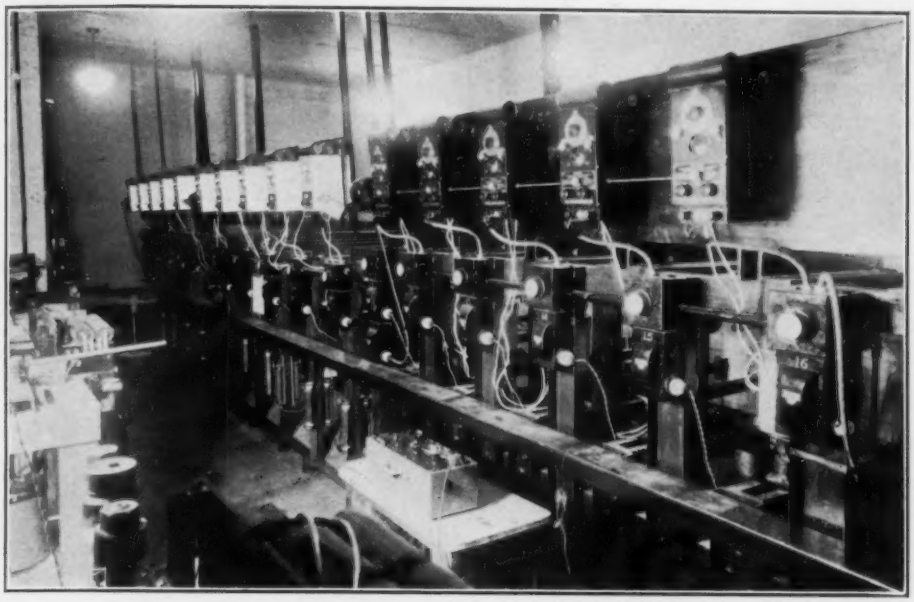


Fig. 2—General View of Heat Control Side of Units.

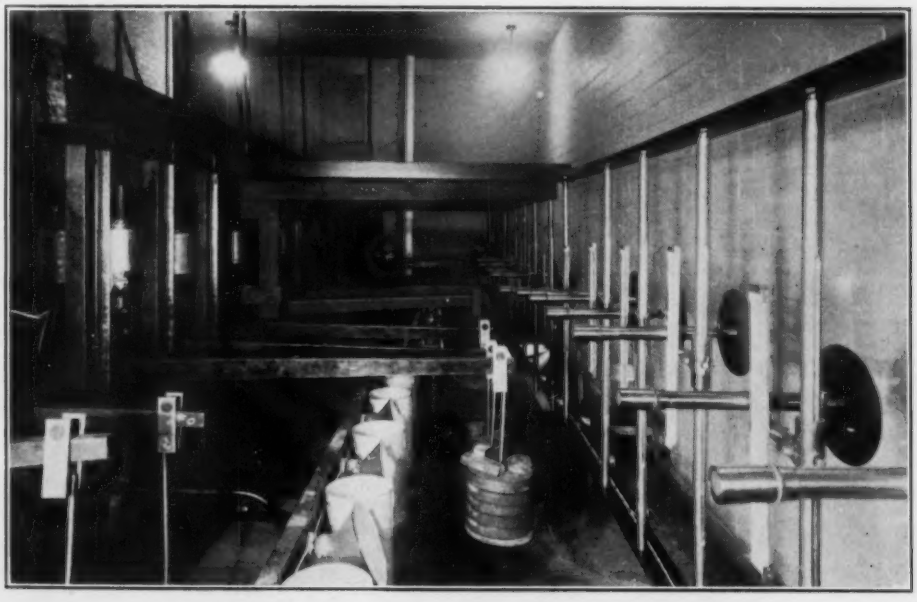


Fig. 3—General View of Flow Test Equipment.

quently used and the results are best expressed in per cent elongation in 100,000 hours. It is true, metals were tested at elevated temperatures previous to 1920, but the work at that time involved but few

niceties with regard to temperature control or exactness of measurements, matters on which, at this time, great stress is laid.

Since it would be beyond the scope of this paper to describe all of the methods employed in making present-day creep tests, only the type of equipment developed at the University of Michigan for this work will be given. It must be understood, however, that these par-

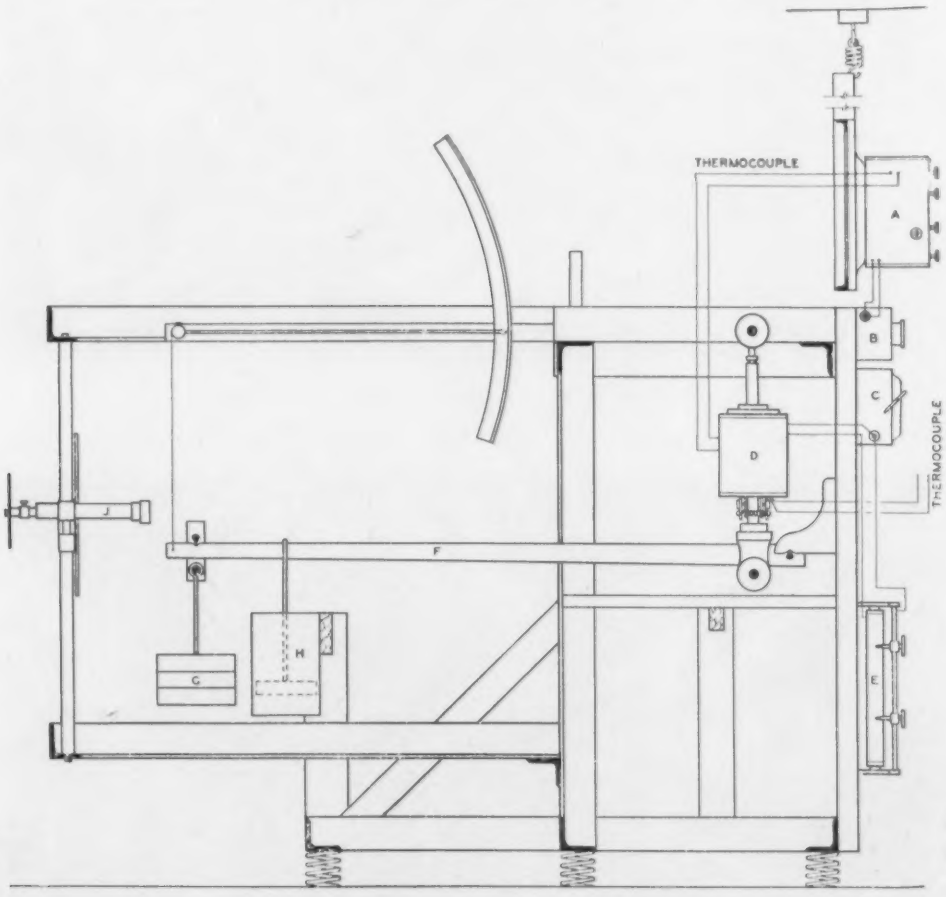


Fig. 4—Diagram of Flow Test Equipment Assembly.

ticular units are by no means the only ones which are proving successful. The general appearance of these units is given in Figs. 2 and 3. An assembly section of the flow test apparatus is given in Fig. 4. The loading device consists of a lever F pivoted at one end and with a test specimen fastened to the lever through a saddle arrangement close to the pivoted end. The load G is applied through another saddle arrangement at the opposite end, and the lever ratio is

such that any applied load is multiplied 24 times at the test specimen. Knife edges are used at all points of bearing.

The test specimen used has a diameter in its reduced section of 0.505 inch and an overall length of 5.5 inches. Consequently, the

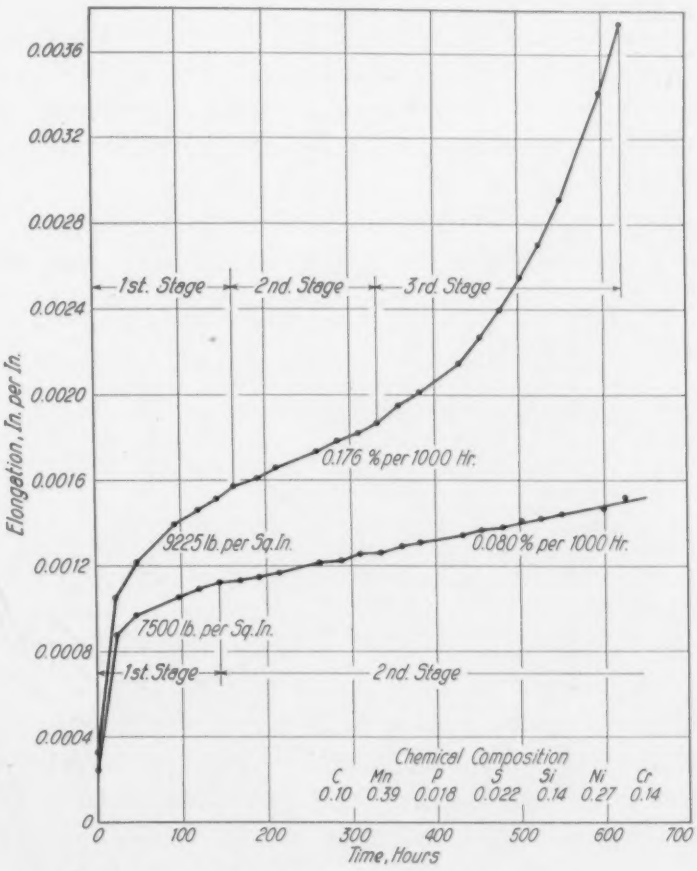


Fig. 5—Time-Elongation Curves for Carbon Steels at 1000 Degrees Fahr. (540 Degrees Cent.).

specimen is not of sufficient length to extend from the lever to the upper support but is screwed into adapters.

The specimen is heated with an electrical resistance furnace, D. The furnace is wound so that the temperature over the entire length of the test specimen is practically uniform. The temperature gradient over the 2-inch gage length should never be greater than 5 degrees Cent.

For holding the temperature constant, a Wilson-Maeulen temperature controller is used for each individual furnace. The control thermocouple is placed close to the furnace winding and a separate

couple is fastened to the test piece itself. External resistances are placed in series with the furnace so that the current may be adjusted to a value just slightly above that required to maintain the furnace at the desired temperature. The automatic control throws off and on the full current.

An optical system is employed for determining any changes in length of the test specimen. The apparatus consists of two parts; one part transfers any eccentric motion of the test piece to some point outside the surrounding furnace, while the other measures any deformation that may occur.

A time-elongation chart resulting from a test is given in Fig. 5. This chart gives the results on a low carbon steel with stresses of

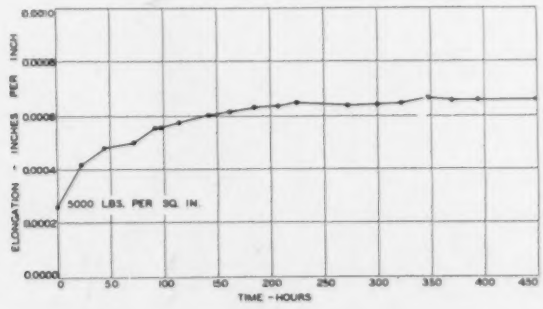


Fig. 6—Time-Elongation Curve for 70-30 Brass at 400 Degrees Fahr. (205 Degrees Cent.)

9225 pounds per square inch and 7500 pounds per square inch respectively. As a result of the stress of 9225 pounds, three known stages of creep are developed. The first is that made up of a combination of elastic and plastic flow in which the rate of elongation is decreasing; the second stage is the one in which the rate of elongation remains constant; and the third stage is the one in which the rate of elongation is rapidly increasing and will so continue until fracture occurs.

One might ask the question as to whether or not the nearly vertical line at the very beginning of the test is a stage. It is usually not so considered but is rather viewed as indicative of the major elastic deformation. Some hold that this deformation thus represented is all elastic, but it is the opinion of the writers that it is made up of both elastic and plastic deformation, though accepting that practically all of it is elastic. On the other hand, the deformations shown in the three stages, especially those in the last two stages, are considered by many to be all plastic in character. In all of these, it

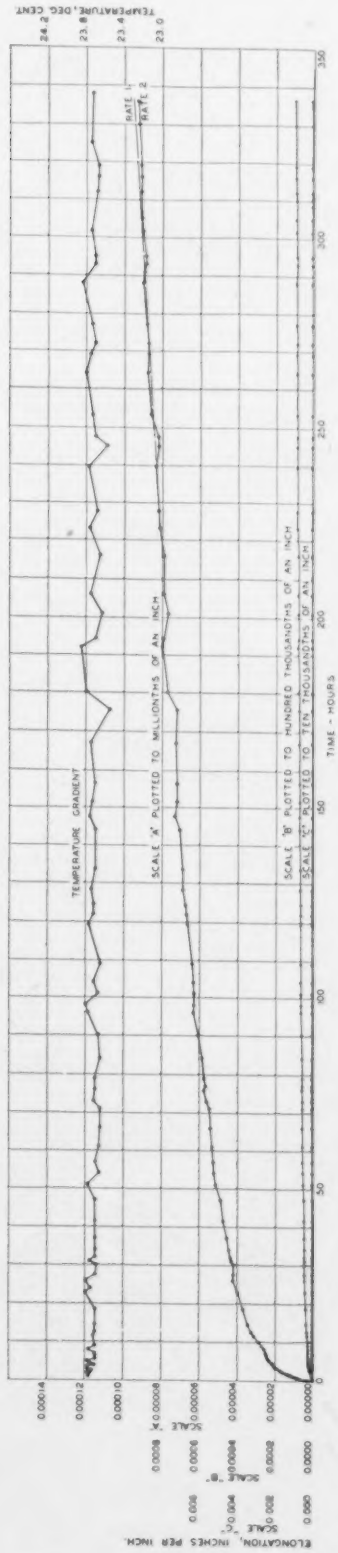


Fig. 7—Time-Elongation Chart for Lead at Room Temperature. Load 200 Pounds per Square Inch.

is probable that although, particularly in the last two stages, the amount of the elastic deformation may be very small both plastic and elastic deformations do exist.

In the curve resulting from a stress of 7500 pounds, there are two stages; one in which the rate of flow is decreasing, and the other in which the rate of flow is occurring at a small, though uniform, rate, with a tendency toward a slight decrease in rate of flow.

The time-elongation curve for a 70-30 brass at 400 degrees Fahr. (205 degrees Cent.) is given in Fig. 6. In this diagram two stages

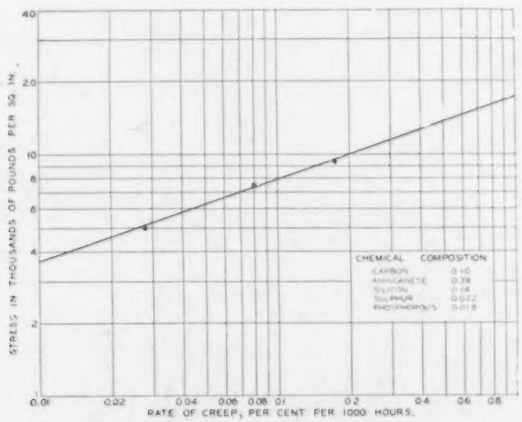


Fig. 8—Logarithmic Plotting of Stress Versus Rate of Creep Produced by that Stress. Carbon Steel at 1000 Degrees Fahr. (540 Degrees Cent.).

of creep can be noted: the first being one in which there is a constant decrease in the rate of creep and the second, one in which the rate of creep in the second stage becomes zero.

Fig. 7 is presented to illustrate the importance of selecting suitable ordinates for plotting. Scale A is plotted to a millionth of an inch, Scale B to one one-hundred-thousandth of an inch, and Scale C to one ten-thousandth of an inch. Were one to attempt to form any judgment as to the flow characteristics of a metal, lead for example, on the basis of plotting to Scale C, one would conclude that no flow was taking place. On the basis of Scale B, a slight, small flow would be detected, though the scale is such that changes in flow due to changes in temperature would not be indicated. On the basis of Scale A, not only is flow recognized, but certain irregularities are found which cannot help but arouse the curiosity of an investigator. These irregularities may be attributed to variations in temperature, which are extremely small, less, in fact, than 0.6 of a degree Cent.

Yet because of the refinements employed in determining elongation, it was possible to observe changes in rate of flow under a constant load of 200 pounds with temperature changes of only tenths of a degree.

Attention is further directed to the importance of using a proper scale to detect a change in rate of creep. On the basis of Scale A, a definite change in rate of creep is noted, whereas, on the basis of Scale B, such change cannot be detected.

It is quite customary to convert the time-elongation curves to a system of logarithmic plotting in order to predict the rate of creep for various undetermined stresses. Thus in Fig. 8, in the case of a 0.10 per cent carbon steel tested at 1000 degrees Fahr. (540 degrees Cent.), it was determined that with a stress of 5000 pounds a rate of creep of about 0.028 per cent per 1000 hours was obtained. With a stress of 7500 pounds a rate of creep of about 0.08 per cent per 1000 hours was obtained. With a stress of 9400 pounds a rate of creep of about 0.175 per cent per 1000 hours resulted. By drawing a line through these points, it is possible to predict the rate of creep for stresses intermediate between the minimum and the maximum ones used, and also, with discretion, to extrapolate the values for the rate of creep in which the stresses employed are less than the minimum or greater than the maximum. This is now the commonly accepted method of plotting data for the purpose of obtaining the rate of creep of metals at various desired temperatures.

Creep testing methods are unstandardized, even after twelve years of intensive work. The type of testing unit used makes quite a difference in the results. As already pointed out, the method of plotting and the specific method of applying the loads are of importance. Work is being done to compare the results obtained by single-step, up-step, and down-step methods of loading. A new test specimen is used for each stress in the single-step method of loading. In the up-step method of loading, only one test specimen is used. It is first subjected to a small stress and is held at that stress until the rate of flow becomes constant or shows a decrease. It is then subjected to a higher stress and this stress is continued until the rate of flow either becomes constant or shows a decrease. This procedure is repeated once or twice more. From the data thus obtained, it is then possible on log-log paper to draw a line which will give the rates of flow for the temperature in question at any stresses possible of determination by interpolation or extrapolation.

The down-step method of loading consists in subjecting the test specimen to a high stress and reducing that stress to one of a lower value and continuing the test at that stress until the rate of flow becomes constant or occurs at a diminishing rate. The stress is then lowered and the same procedure is repeated. This is continued for three or more times, after which it is possible to plot the results of the data. The work which has been done to date at 850 degrees Fahr.

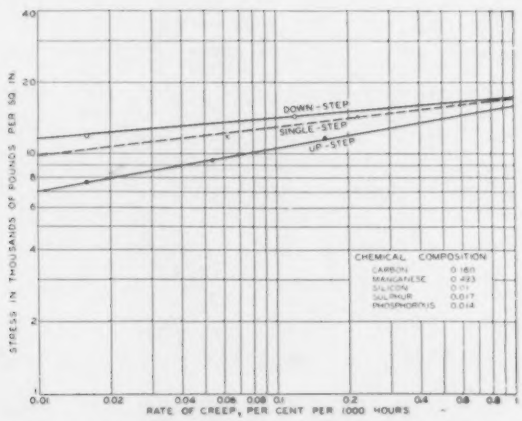


Fig. 9—Influence of Method of Loading on the Creep Characteristics of Grade A Steel at 850 Degrees Fahr. (455 Degrees Cent.).

(455 degrees Cent.) on these three methods of loading shows that the up-step method of loading for the same stress gives higher rates of creep than those obtained with either the single-step or the down-step method of loading. The comparison further shows that the lowest rates of creep are obtained from down-step loading and that intermediate rates of creep result from the single-step method of loading as is shown in Fig. 9.

Although there were no exact data to substantiate it, a relationship between the method of loading and the creep characteristics was predicted from theoretical considerations for the temperature in question. The explanation of this relationship follows:

Metal, when tested at or below the equicohesive temperature, which is the lowest temperature of recrystallization, will, if in a severely strained condition, have many small crystals or fragments of crystals. These small crystals, especially those in the grain boundaries, should decrease the rate of creep. The down-step method of loading produces this condition most ideally. Therefore, it would be

assumed that such a method of loading would have the lowest rate of creep. The experimental results proved this to be the case.

In the up-step method of loading, less overstraining for a given stress would take place. Therefore, there would be fewer crystalline fragments with a consequent increase in rate of flow over and above that resulting from the down-step method of loading. The results showed that this, too, was the case.

In the single-step method of loading, the rate of load application should tend to be greater for a given stress than it would be in the up-step method of loading. This would be particularly true when

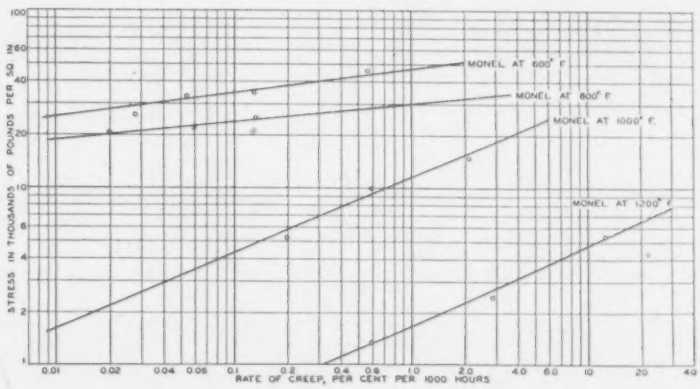


Fig. 10—Creep Stress Diagram for Monel Metal.

two or more stresses had been used in the up-step method of loading, whereas to reach the same last stress but one application had been used in the single-step method. The increased rate of load application would tend to produce more crystallites. These would tend to decrease the rate of creep when compared with the rate of creep resulting from the up-step method of loading. Investigation proved this to be true. Since the amount of strain hardening for given conditions would be less than in the down-step method, the rate of creep should tend to be more than that resulting from the down-step method. This conclusion was borne out by the experimental results.

A matter of two or three years ago, the present writers propounded the theory that the logarithmic plotting of stress versus rate of creep would, for the same metal at all temperatures below the recrystallization temperature, give lines that were essentially parallel to one another and that, at temperatures above the recrystallization temperature, the same condition would exist, although the lines resulting from temperatures above the recrystallization temperature would not

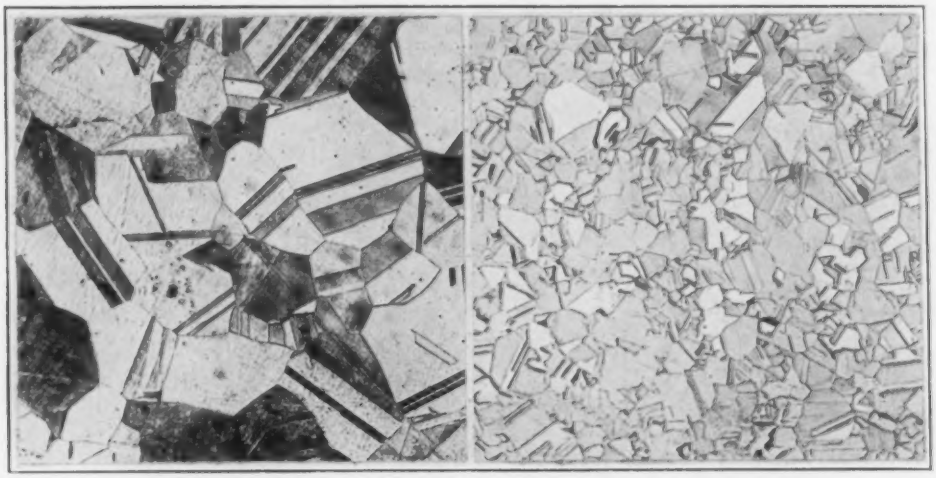


Fig. 11A—(Left) Coarse-Grained 77-22-1 Alloy, As-Received.
Fig. 11B—(Right) Fine-Grained 77-22-1 Alloy, As-Received.

necessarily be parallel to those resulting from the use of temperatures under the recrystallization temperature. This hypothesis was somewhat at variance with one advanced by another authority on this sub-

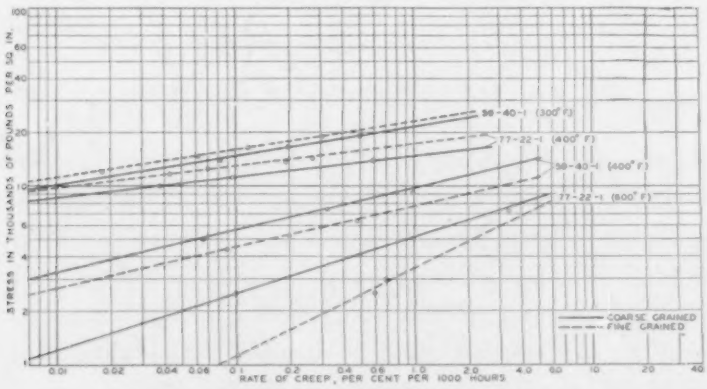


Fig. 12—Creep Stress Diagram for Copper-Zinc-Tin Alloys Showing the Influence of Grain Size on Rate of Creep.

ject, who stated that for all temperatures the lines resulting from a plotting of the log of stress versus the log-rate of creep would be parallel.

In support of this theory of the present writers, the rate of creep for Monel metal at 600, 800, 1000 and 1200 degrees Fahr. is given in Fig. 10. The tests at 600 and 800 degrees Fahr. (315-425 degrees Cent.) are below the recrystallization temperature and the resultant lines of the tests at these respective temperatures are essen-

tially parallel. The test at 1000 and 1200 degrees Fahr. (540-650 degrees Cent.) are above the recrystallization temperature and these lines are approximately parallel to one another. It will be noted, as expected, that for a given rate of creep the stress is lower with increasing temperature. Thus, to produce a rate of creep of 0.6 of one per cent in a thousand hours at 1200 degrees Fahr. (650 degrees

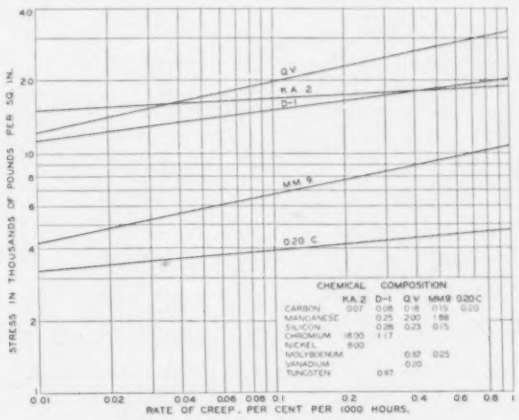


Fig. 13—Effect of Composition on the Creep Characteristics of Steels at 1000 Degrees Fahr. (540 Degrees Cent.).

Cent.), a stress of but 1400 pounds would be required; whereas, at 600 degrees Fahr., a stress of approximately 44,000 pounds would be needed.

Another theory which has been advanced by the present authors is to the effect that the rate of creep would be less for fine-grained metals than for coarse-grained metals when at temperatures below the recrystallization temperature, and that the reverse would be true or that the rate of creep would be less for coarse-grained metals than for fine-grained metals for temperatures above the recrystallization temperature. These conditions are shown in Figs. 11 and 12. Fig. 11 presents photomicrographs of a coarse and a fine-grained brass consisting of 77 per cent of copper, 22 per cent of zinc, and 1 per cent of tin. This particular brass was subjected to creep tests and the resulting data are shown in Fig. 12.

Both of the hypotheses just stated are based on the factors causing and interfering with the creep phenomenon which are as follows. Between the crystals of the metal is a cement-like product which has been described as amorphous but which is now generally considered to be submicroscopically crystalline. At room temperatures, as

shown by fracture tests, this product is stronger than the large crystals. This holds true up to the recrystallization temperature. Above that range, however, it was felt that the large crystalline masses offered a better resistance to plastic flow than the small crystalline aggregates. The data just presented would confirm this point of view.

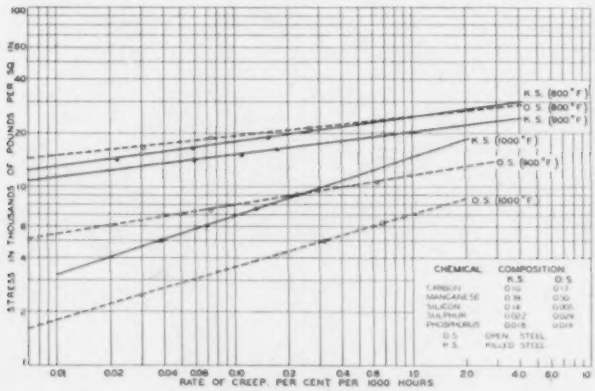


Fig. 14—Creep Stress Diagram of Open and Killed Carbon Steels at 800, 900 and 1000 Degrees Fahr. (425, 480 and 540 Degrees Cent.).

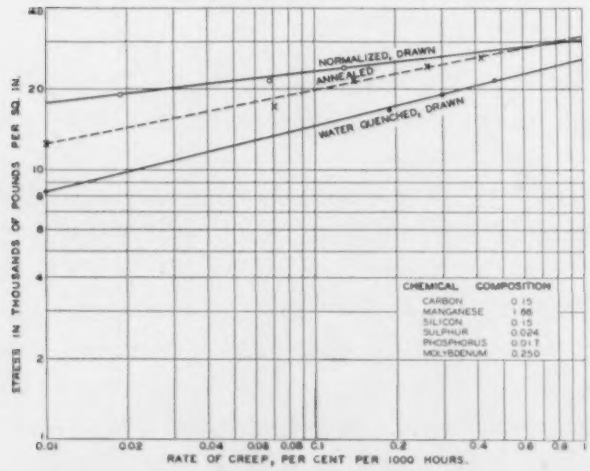


Fig. 15—Effect of Heat Treatment on the Creep Resistance of Steel MM9 at 900 Degrees Fahr. (480 Degrees Cent.).

Were it otherwise, there would have been no change in the slope of the lines in Fig. 10 as the test temperatures changed from those below the recrystallization range to those above. Further, there would have been no reversal of the creep relationship as shown in Fig. 12. That is, the fine-grained brass might have shown a lower rate of

creep at temperatures above, as well as those below, the recrystallization range.

Various metals have various rates of creep. The ferrous metals as a class have the lowest rate of creep. Of these, an 18 and 8 alloy, consisting of 18 per cent chromium and 8 per cent nickel and known as stainless steel, has shown at high temperatures a very low rate of creep. By high temperatures, are meant temperatures such as 1200 and 1300 degrees Fahr. (650-705 degrees Cent.). At lower temperatures, the creep characteristics of ferrous metals tend more nearly to approach one another. The creep characteristics of a number of steels at 1000 degrees Fahr. are given in Fig. 13. This chart shows that plain carbon steel possesses the lowest stress for a given rate of creep and that steels designated as D-1, QV, and KA2 show high stress for a given rate of creep. Steels D-1, a chromium-tungsten-silicon steel, and QV, a manganese-molybdenum-vanadium steel, were developed in the laboratories of the University of Michigan for the purpose of making available for engineering purposes steels that will have good creep characteristics up to 1100 degrees Fahr. (595 degrees Cent.) at a reasonable price.

Not only has it been found that composition plays an important part in determining the creep properties of metals, but methods of manufacture should also be considered. This is especially true of open versus killed steels when tested above the equicohesive temperature. Open steel is not treated with a final oxidizing agent such as silicon or aluminum. The gases it contains are distributed throughout the metal. Killed steel, on the other hand, is degasified and hence is more dense than steel made by the open process. It would be assumed, therefore, that the more dense steel would have the lowest rate of creep. This is found to be the case at temperatures of 900 and 1000 degrees Fahr. (480-540 degrees Cent.) from the data given in Fig. 14 for an open and for a killed steel. It has also been found that heat treatment, particularly in ferrous metals, appreciably affects the resultant creep characteristics. The lowest rates of creep for temperatures above those of recrystallization usually result from a normalizing treatment, followed by a high draw. A high draw here signifies reheating of the steel to about 1200 degrees Fahr. (650 degrees Cent.), followed by a cooling in still air. The difference in the creep characteristics of a low-alloyed steel when subjected to three different types of heat treatment is given in Fig. 15. In this

it will be observed that the lowest rate of creep is obtained from the normalized and drawn stock.

These findings are not wholly unexpected when viewed in the light of our knowledge of the nature of crystals and crystalline aggregates and the effects of the properties of the various constituents in these steels. The quenched and drawn stock, because of its heat treatment, would have no crystals of any considerable size. Assuming that maximum creep at temperatures above the equicohesive is a function of crystal size and composition of crystal, then for a given metal that heat treatment which produced crystals of appreciable size would give the best creep properties. This was found to be the case since the results of normalizing and annealing treatments, both of which would give crystals of larger size than the quenching treatment, gave superior creep properties. That the normalized steel possesses superior creep properties to annealed steel is not so simple of explanation. Presumably, the annealing treatment should give larger crystals than a normalizing treatment. Metal thus treated, therefore, should, when at temperatures above the equicohesive, have a lower rate of creep. This was not found to be the case and a probable explanation is that the constitutional composition of the crystals may have played a part in the results since the crystals were in both cases of nearly the same size.

Possibly no development in recent years in the metallurgical field has done more to ground metallurgy in fundamentals than the studies and investigations in the field of creep. This work has raised testing methods to the highest degree of precision and it is causing metallurgists to constantly query with respect to the nature and constitution of matter.

DISCUSSION

Written Discussion: By Dr. H. S. Rawdon, chief, Division of Metallurgy, U. S. Bureau of Standards, Washington, D. C.

The authors have given us a very clear presentation of current testing procedure for determining the creep of metals at elevated temperatures and the principal facts which have been established in the past 12 years, since intensive research along this line was undertaken, have been summarized in this concise and readable presentation.

To the writer, the point of greatest interest discussed by the authors is the marked difference in rate of creep at a chosen temperature which may be obtained for any material according to the method of loading used. Creep testing of a material, at the best, is time-consuming and expensive. The desire to ex-

pedite the test by using a single specimen for securing all the data required for any chosen temperature is a natural one and many workers have followed this line of attack. It is evident, however, from the authors' data (Fig. 9) without further comment, that some arbitrary agreement as to the method of loading to be used must be reached. The situation is quite analogous to that which existed several years ago with respect to the determination and significance of "elastic limit" in ordinary tension testing. The need for specifying the method and procedure for determining the elastic properties of a material, irrespective of the name used for their designation, has been so strongly emphasized that ignorance on the part of testing engineers on this point is now inexcusable.

The data presented by the authors on the method of applying the load are of interest from another viewpoint. Only rarely in service does the condition in a stressed member approximate at all closely the relatively simple condition which obtains in a bar under load in a testing machine. In high temperature service, this statement is still more applicable than in service in which temperature is not an important factor. The laboratory rate of creep, as determined by the "single-step" method of loading, for example, need not necessarily represent actual service conditions. Indeed, in a set-up which is being "pushed" in order to increase the output, the data obtained by the "up-step" method of loading might be more applicable. At any rate, the authors' data serve a very useful purpose in emphasizing the variations in the rates of creep resulting from accompanying variations in the loading method.

The explanation advanced by the authors for these observed differences in creep rate is not so convincing to the writer, however, as the experimental data are. So long as the temperature at which a test is carried out does not exceed that of recrystallization of the metal, it is not apparent why there should be any structural changes with which to correlate the observed changes in creep. The matter appears to be one of great significance in creep testing both from the practical and the theoretical aspect. Additional confirmatory work by other workers would seem to be justified by the importance of this phase of the general subject of the creep of metals.

Written Discussion: By John J. B. Rutherford, U. S. Steel Research Laboratories, Kearny, N. J.

The new results presented by the authors, which are in general harmony with the data of previous investigators of phenomenon of creep, raise a number of questions. The comparison of the different methods of loading is interesting, although it would seem that the initial load by the up-step method of loading ought to produce a rate of creep identical with that produced by the same load in the single-step method; additional loading would produce a difference in rate of creep by the two methods, as has been found. Possibly, had the authors repeated the measurements, they might also have observed this, in which case the slopes of the lines in Fig. 9 would have to be changed, and their inferences would have to be modified.

The curves of Fig. 13 show a considerable difference in creep rate between steels QV and MM9, which, however, are almost identical in stated composition, except for the presence of 0.20 per cent vanadium. It is rather surprising

that this small proportion of vanadium should suffice to lessen the rate of creep to one-hundredth; further information on this point would be welcome.

It may be of interest to note that the rate of creep of 18-8 alloy, which, as is well known, is remarkably low, appears to be appreciably greater, even at temperatures of 1200 degrees Fahr., for specimens which have been cold-worked than for similar specimens when thoroughly annealed.

Written Discussion: By G. R. Brophy, research laboratories, General Electric Company, Schenectady, N. Y.

In this paper the authors present a clear discussion of the fundamentals of creep, and the influence on the results of factors which are too frequently overlooked, both by designers and testers.

The method of loading is very important, as has been pointed out previously by Kanter and Spring, and the writer. Misleading results are obtained if this fundamental is disregarded. Probably the best method of loading is, as the authors term it, the single step. It at least is the only way that consistent results and checks can be obtained especially between laboratories.

The reader may obtain the impression from the authors' statement at the end of paragraph 1, page 10, that up-step loading always gives the highest rates and down-step the lowest rates, with intermediate rates for the single-step method. This is probably true for the particular steel of Fig. 9 and at the temperature of test, but the question arises, "At a lower temperature would not the single-step yield the highest rate of creep, with the step-up method giving an intermediate rate?" This was indicated by the writer in his own work, some of which was presented last year. It is believed that the relation of the test temperature to the "equicohesive" temperature will determine the order of creep rates for the different methods of loading, though apparently the down-step method always produces the lowest rates at temperatures below and slightly above the "equicohesive" temperature.

The writer prefers the term "strain hardening temperature limit" to the "equicohesive" temperature in this connection, because of other possible factors in the rate change of creep, for instance, precipitation hardening under the influence of strain at temperature.

It has always been a question with the writer that a consideration of a creep rate is accurate, and that the assumption of the creep rate at the end of any period, say 300 or 400 hours, represents the creep rate at the end of 100,000 hours. As usually determined, this latter rate is probably safe but not at all economical. It seems that a consideration of total creep under any set of conditions would be better, and this may be calculated from the equation of any creep curve, at least those constructed from data obtained below the strain hardening temperature limit.

It has been shown that the straight line relation between stress and strain (creep) holds, at least for temperatures below the strain hardening temperature limit. Therefore, the strains after any time interval (calculated to 100,000 hours) for two or more test loads plotted against those loads, should give the designer an accurate means of estimating the creep at lower design loads.

Written Discussion: By C. R. Austin, associated with research laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh.

The authors are to be congratulated on publishing another of their instructive papers on the creep of metals at elevated temperatures. The paper is particularly valuable in that it focuses the attention of metallurgists on an important avenue of approach for the consideration of the nature and constitution of metallic substances.

Of particular interest are the data furnished on the up-step, single-step and down-step methods of establishing creep rates. The writer has recently been particularly interested in the effects of these various methods of approach as revealed in the Rohn type of test, and has run several tests on pure metals. It is hoped that the data will be published at an early date.

The authors appear to confuse the terms temperature of recrystallization and equicohesive temperature. While it has been stated that the equicohesive temperature generally corresponds closely with the temperature of recrystallization the terms are by no means synonymous.

In attempting to explain the stress-rate of creep curves obtained by the three aforementioned methods, it is considered that the authors become a little involved. No history of the treatment of the metal previous to testing appears to have been given, but it is assumed that the data for grade A steel (Fig. 9) were obtained on annealed specimens. If such is the case, it would seem that the up-step test would provide the least strain on the test piece for the given temperature and hence the least amount of hardening. A given rate of creep would, therefore, be obtained with the minimum stress. By the down-step method, the initial load causes relatively greater hardening, so that rate of creep for any given load is decreased.

To the writer the additional introduction of crystal fragmentation as an explanation of the phenomenon exhibited does not appear to be desirable. Fragmentation usually implies much more crystalline distortion than presumably takes place during the earlier stages of creep testing—at least before the third stage of the test is reached. During the second stage, which follows the almost completely elastic first stage, the total amount of deformation is extremely small, and of the order of 0.04 per cent (see Fig. 5). This amount of deformation would not even show crystal distortion under the microscope.

It should be noted that the order of the curves presented for grade A steel in Fig. 9 results from data obtained below the recrystallization or softening range (455 degrees Cent.). I should like to ask the authors if they do not consider that a complete reversal of location would be obtained if the temperature were raised to somewhere in the recrystallization range. Possibly they have some experimental evidence to cover this point.

Again in referring to normalized and annealed steel the authors indiscriminately employ the term—equicohesive temperature when they apparently mean temperature of recrystallization. The persistence of strain in a metal undoubtedly hardens the material and this, in turn, increases the resistance to plastic flow. Furthermore, the less the strain the higher the temperature to which the metal must be heated before the strain is removed. Thus, in the writer's opinion, it is perfectly rational that at 480 degrees Cent. the normalized sample should exhibit creep properties superior to the annealed sample.

The writer would also like to add a word on the theory advanced to ex-

plain the difference in behavior of fine-grained and coarse-grained metals at elevated temperatures. The authors of the paper state that "between the crystals of the metal is a cement-like product, which has been described as amorphous, but which is now generally considered to be submicroscopically crystalline." As the authors have used Rosenhain's theory of intercrystalline amorphous cement to explain the experimental differences obtained above and below the equicohesive temperature (where the strength of the crystalline material approximates to that of the amorphous material), it seems a little inconsistent to later abandon that phase and interject "sub-microscopic crystals."

The data plotted in Fig. 12 show a remarkable consistency in the superiority at high temperatures and inferiority at low temperatures in the creep resistance of coarse-grained in comparison to fine-grained material. In the 77-22-1 alloy, however, the log stress—log creep rate curves for the fine and coarse-grained alloy appear to intersect at a stress of 10,000 pounds per square inch when the rate of creep has reached about 10 per cent per 1000 hours. Does the explanation of this lie in the fact that the rate of deformation is approximating to some high rate where the amorphous cement exhibits a strength equal to that of the crystals, due to this high rate of testing, and hence renders the influence of amount of amorphous phase immaterial on the total creep strength of the alloy?

The writer has studied the paper with much interest and looks forward to further stimulating work along the lines of the present paper.

JEROME STRAUSS:[1] I would like to say a word with reference to the note of surprise expressed by Mr. Rutherford. Is it so surprising that vanadium should contribute to high temperature strength in view of two very well known facts:—the first very clearly emphasized by Dr. Reed in a paper presented at a meeting of the Society last year in which he showed that vanadium is the most powerful of the carbide-forming elements commonly associated with iron; the second fact known to us through long years of experience with high speed steel and cast iron, that vanadium is very powerful in delaying the agglomeration and decomposition of the carbides existing in iron-carbon alloys.

Authors' Closure

We wish to express our appreciation to the various gentlemen who have been so kind as to discuss our paper. One of the main purposes of presenting papers of this type is to create discussion and in this case we feel our efforts have been rewarded.

Referring first to the comments of Dr. Austin, we are in agreement in feeling that there is not a definite relationship between the equicohesive and recrystallization temperature. We do feel, however, that the equicohesive temperature and lowest temperature of recrystallization are one and the same thing. Throughout this paper we have used recrystallization temperature to mean the lowest recrystallization temperature. Recrystallization temperature in itself has no meaning whatsoever as there are many factors which influence it. On the other hand, we feel that every metal or alloy of a given composition has a definite equicohesive or lowest temperature of recrystallization and that the

[1]Chief research engineer, Vanadium Corporation of America, Bridgeville, Pa.

resulting creep characteristics are closely related to this apparently critical temperature.

Partly on the basis of definition, we feel that the terms equicohesive and low temperature of recrystallization are identical. Our definition of equicohesive temperature is that temperature at which the grain boundaries possess sufficient mobility to allow deformation and thus fracture to occur on the boundaries. The definition for lowest temperature of recrystallization is the lowest possible temperature at which recrystallization may (not necessarily does) occur under the most favorable conditions, which implies that the grain boundaries possess sufficient mobility to allow the grains to re-orientate themselves at the boundaries.

The results which have been presented as to the effect of method of loading were, of course, intended to apply only to the particular steels at the particular temperatures considered. Similar conditions may not exist at other temperatures for these same steels, or for other steels even at these temperatures. Much additional work remains to be done before the present findings may be extended too broadly.

Mr. Rutherford raises the question as to the remarkable influence of vanadium on increasing the creep resistance of manganese-molybdenum steels. We have found this to be true not only in the case of this particular type of steel, but also in the case of many other steels that have been considered to date. This is especially true of steels which are commonly used for bolting material for high temperature applications, such as those of the chromium-tungsten type.

Not only vanadium but certain other elements as well exert a very marked influence when small amounts are added, or when the amount present is slightly changed. We recently had occasion to investigate a series of 50 alloy steels all of which contained exactly the same three elements but in which the amount of these elements present was varied by 0.50 per cent increments. It is often startling to see the great change in creep characteristics that may be produced by relatively slight changes in the amount of the alloy present. It seems that there is a critical amount of each element which must be present in order to exert the maximum creep characteristics and moreover that the amount necessary varies depending on what other elements may be present.

Mr. Rutherford also points out the fact that in single-step and up-step loading the same rate of creep should be obtained under the initially applied load. Such would, of course, be the case if it were not for the time factor. In the so-called up-step method of loading, the initial stress is maintained for a period of 400 to 600 hours, while in the single-step method, the initially applied load may be maintained for a period as long as 2000 hours.

In closing we wish to state that the factors which we have presented in this paper are not by any means the only ones which influence the creep of metals at elevated temperatures. Since this publication we have investigated many additional factors and many more remain to be considered, some of which have as much bearing on the creep characteristics as those which have been considered in this paper.

FURTHER STUDIES ON CHROMIUM-NICKEL-IRON AND RELATED ALLOYS

By Vsevolod N. Krivobok, With the Assistance of E. L. Beardman, H. J. Hand, T. O. A. Holm, A. Reggiori and R. S. Rose

Abstract

The present investigation deals with the theoretical considerations concerning the chromium-nickel-iron-carbon constitutional diagram, with factors influencing the existence of metastable phases, and, in consequence of the latter, with the so-called "decomposition" or "disintegration" of these alloys. Such decomposition is known to be accompanied by the precipitation of a constituent generally believed to consist of carbides. It is suggested that the precipitated constituent is not necessarily a carbide: in fact, in very low carbon alloys, the precipitated constituent is, undoubtedly, magnetic chromium-nickel ferrite. That is to say, the nature of a separating constituent is dependent upon the carbon content of the alloy.

A phase change, from nonmagnetic to magnetic, accompanies decomposition. Whether decomposition precedes phase change or follows it is a matter of conjecture.

The alloys were studied by means of magnetic analysis, microscopic observations, and corrosion tests. Alloys of extremely low carbon content, in which no carbide precipitation could take place, are described and shown to be immune from decomposition. When carbon is increased above a certain, very small amount, the decomposition process is practically independent of the carbon content, and consequently there is very little reason to aim at the low carbon content in commercial alloys.

A large number of chromium-nickel-iron alloys with the addition of other elements (such as cobalt, molybdenum, silicon, copper) are described from the point of view of their behavior when subjected to decomposition treatment. It was found that the additions of certain elements prevent phase change, but do not suppress precipitation of a constituent, presumably, carbides.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, Dr. Vsevolod N. Krivobok, a member of the society, is metallurgist, Bureau of Metallurgical Research, and professor of metallurgy, Carnegie Institute of Technology, Pittsburgh. The co-authors are all graduate students of that Institute. Manuscript received June 20, 1931.

The greater the amount of special additions the lower is the upper limit of decomposition range.

It has also been shown that, contrary to ordinary chromium-nickel-iron alloys, such precipitation has but little effect on some of the mechanical properties and resistance to corrosion in standard acid solutions, although the so-called copper sulphate test shows these alloys to be equally susceptible to attack. On the strength of this study, a suggestion is made that copper sulphate tests should be applied with intelligence.

Changing the relative amounts of chromium and nickel in the alloy, as for example using 12 per cent nickel and 12 per cent chromium instead of 18 per cent chromium and 8 per cent nickel, does not improve the alloy from the point of view of decomposition.

The resistance to decomposition of alloys with special additions seems to be materially influenced by carbon content. The general indication is that the higher the carbon content, the larger must be the additions of those elements, which have been found to be beneficial.

The influence of the treatment which the alloys received previous to the decomposition treatment is fully described. Original quenching temperature of the alloy exercises a very definite influence on decomposition. Alloys of different carbon content of the general "18-8" composition can be divided into three groups, each group with definite magnetic characteristics after decomposition treatment.

Numerous curves showing the relationship between different properties of decomposed alloys are presented.

I. Introduction

THE present widespread application of chromium-nickel corrosion-resistant alloys bears testimony to the usefulness of their properties and indicates immense possibilities.

There are, however, two limitations which have been discussed rather widely, one of them intergranular attack by corroding gases at high temperatures[1], and the other grain-boundary "decomposition" or "disintegration" which occurs when the sample has been heated for some time at 1000 to 1500 degrees Fahr.[2]

[1]Work along these lines has been in progress during the last year and although the results are not available for publication as yet, the preliminary progress report can be obtained by those interested by applying to Dr. V. N. Krivobok.

[2]H. D. Newell reports the temperatures as 880 to 1800 degrees Fahr.

The mechanism of this latter intergranular decomposition has been the subject of a number of studies[3]. A commonly voiced opinion as to the manner of decomposition involves the belief that at the reheating temperatures around 1300 degrees Fahr. there is excess carbide due to the steel being hypereutectoid; that in precipitating, the carbon associates with itself an unduly large proportion of chromium; that this chromium is drawn from the grain boundary areas which immediately surround the carbide; and finally that as a result, these areas with their reduced chromium content are less resistant to corrosion.

It is our belief, however, that this matter deserves further study, since photographs Figs. 2 and 3 show a steel with only 0.01 per cent carbon, which was etched by Murakami solution (which attacks carbides), as compared with photographs Figs. 1 and 4 which show an ordinary 18-8 heated to near the peritectic temperature and a straight chromium steel quenched from a high temperature.

It should be pointed out that although the decomposition is *most pronounced* at the grain boundaries, it takes place within the grains as well, as shown in photograph Fig. 5.

In 18-8 alloys the carbide precipitation at 1300 degrees Fahr. is accompanied by the appearance of magnetic constituents whose presence is ascribed to transformation of austenite, this transformation being in turn ascribed to a lowering of the stability when the chromium is withdrawn from the solution and precipitated in the carbide.

When it was observed that the alloys became less resistant to corrosion and at the same time became magnetic, it was perhaps natural to seek a relationship between the magnetic properties and the corrosion resistance. Indeed such a relationship was found to hold in the case of certain 18-8 alloys with various carbon contents. However, it soon became apparent that the corrosion phenomena depended on the extent of the carbide precipitation, whereas the magnetic phenomena depended on the amount of alloys, especially nickel, which might preserve the alloy nonmagnetic and yet permit it to show the corrosion phenomena.

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[3]H. H. Lester, TRANSACTIONS, American Society for Steel Treating, Vol. 16, No. 6, 1929, p. 743. B. Strauss, H. Schottsky and J. Hinnuber, *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 188, March 1930, p. 309. Also *Metals and Alloys*, Vol. 1, No. 16, Oct. 1930, p. 785. R. H. Aborn and E. C. Bain, TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 837. V. N. Krivobok and M. A. Grossmann, TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 808.

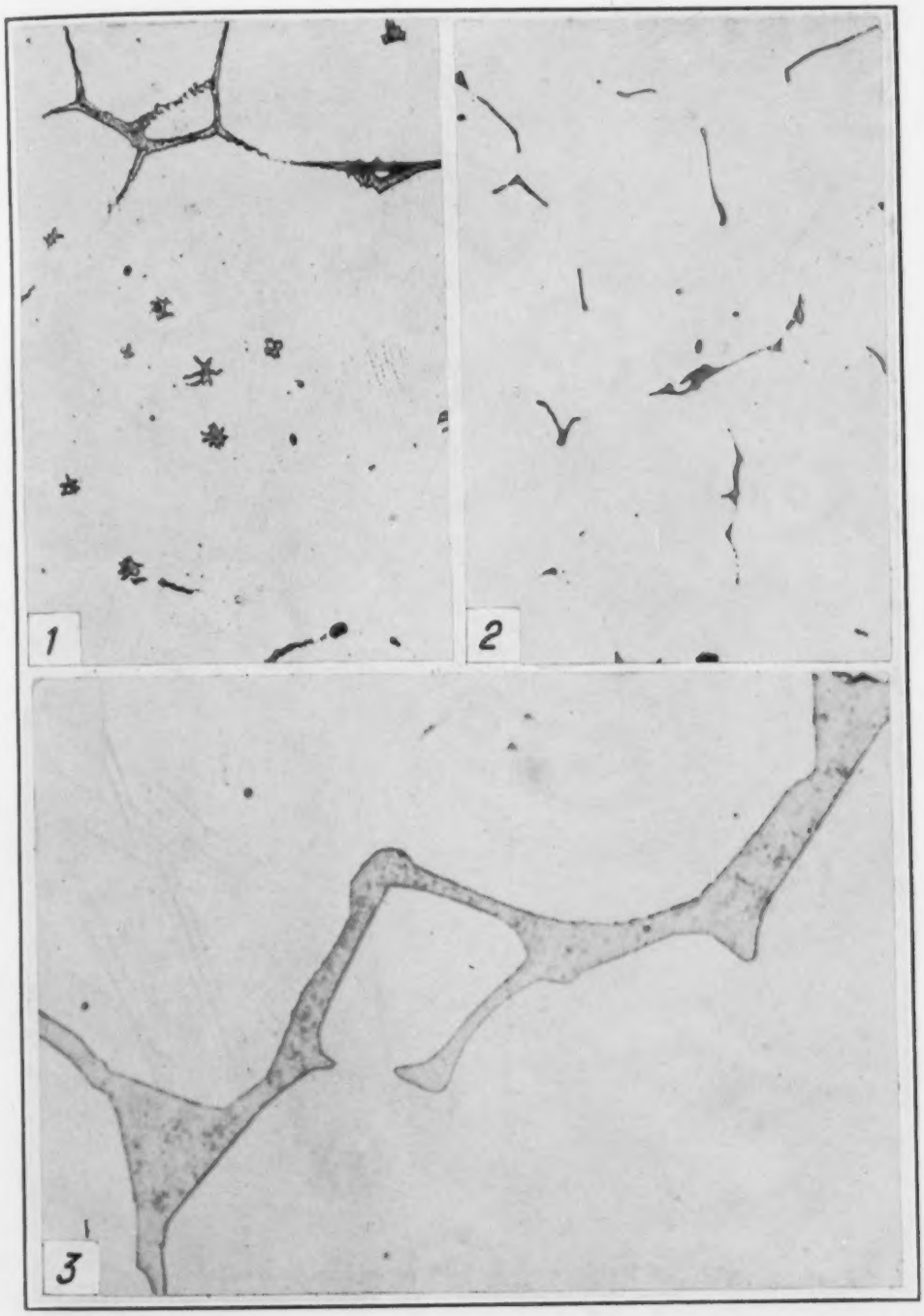


Fig. 1—Chromium-nickel Alloy (18-8) Heated to High Temperature and Etched with Murakami Reagent. × 250.

Fig. 2—Alloy No. 18-8-1 Showing the Structure of the Alloy As-cast. Etched with Murakami Reagent. × 250.

Fig. 3—Alloy No. 18-8-1. Same Specimen as Fig. 2 Magnified × 2500. Scratches Show that Both Constituents have Approximately the Same Hardness.

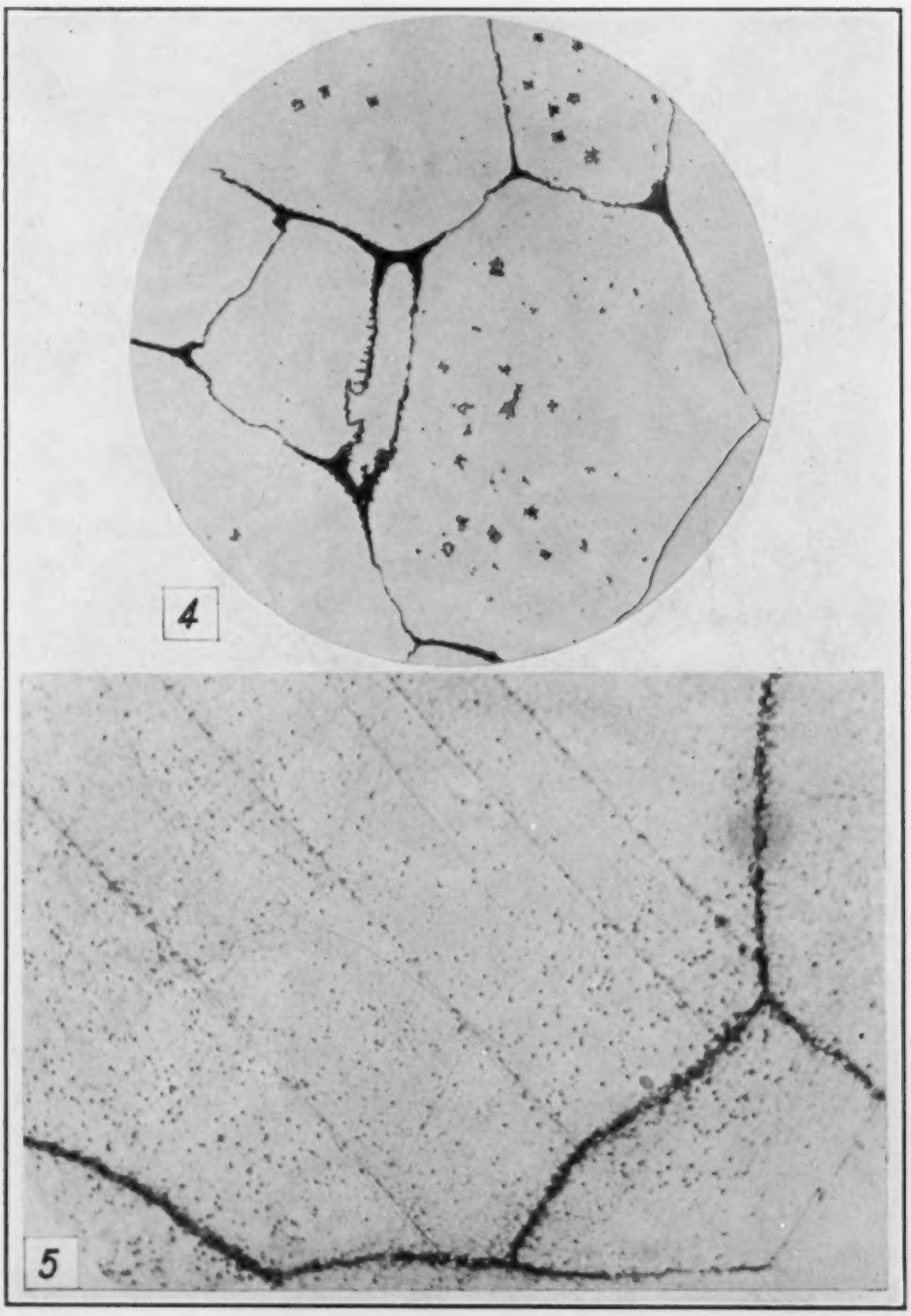


Fig. 4—Alloy Containing 21.4 Per Cent Chromium and 0.62 Per Cent Carbon, Heated to a Temperature Where Peritectic Reaction Should Take Place. Etched with Murakami Reagent. × 250.

Fig. 5—Decomposed 18-8 Alloy. Note Decomposition at Grain Boundaries as Well as Within the Grains. Etched with Murakami Reagent. × 2500.

Table I

Charpy Impact Test Values

		Analysis of Steel Used Per Cent								
		Cr	Ni	C	Mn	Si	P	Cu	Mo	S
Steel No. 1		18.14	7.91	0.15	0.40	0.32	0.018			0.018
Steel No. 2		18.90	8.81	0.13		0.48		1.17	0.95	
Steel No. 3		18.21	9.06	0.19				1.02	0.97	

		High Temperature Quench in Water Treatment		Low Temperature Air Cooled Treatment					
Treatment		Temperature of	Time at Temp. Hrs.	Temperature of	Time at Temp. Hrs.	Charpy Impact Test Values			Average
Steel No. 1	1	2100*	½			57.4		53.6	55.5
	2	2100*	½			73.0		no break	73.0
	3	2100	½			no break		no break	
	4	2100	½	1700	100	66.7		70.2	68.5
	5	2100	½	1400	100	21.1	24.1	22.3	22.5
	6	2100	½	1200	100	54.8	44.6	44.5	48.0
	7	2100	½	1000	100	67.3	64.8	57.6	63.2
Steel No. 2	8	2100	½	none		67.2		no break	70
	9	2100	½	1700	100	.....			....
	10	2100	½	1400	100	35.6		34.2	34.9
	11	2100	½	1200	100	58.3		56.5	57.4
	12	2100	½	1000	100	65.5		65.8	65.7
Steel No. 3	13	2100	½	none		51.4		42.2	46.8
	14	2100	½	1700	100	.....			....
	15	2100	½	1400	100	31.4		29.2	30.3
	16	2100	½	1200	100	48.4		55.0	51.7
	17	2100	½	1000	100	54.7		50.9	52.8
	18	2100	½						

*Instead of quenching, sample No. 1 was furnace cooled and sample No. 2, air cooled. (R. T. Tindula, in author's laboratory)

Table II

Mechanical Properties of 18 Per Cent Chromium, 8 Per Cent Nickel Alloy

Condition or Treatment	Carbon Content	Ultimate Strength (Lb. per sq. in.)	Yield Point (Lb. per sq. in.)	Elongation (Per Cent in inches)	Reduction of Area (per cent)	Brinell Hardness	Charpy Impact
8,930 hrs. 920° F oil outlet	0.04	101,500	39,000	42.5	36.4	149	50
several 1000 hrs. 920° F oil outlet	0.05	94,750	39,800	37.5	43.0	146	85
10,200 hrs. 920° F oil outlet	0.05	96,200	38,900	41.0	32.6	152	57
10,200 hrs. 920° F oil outlet	0.05	92,300	37,800	41.0	31.6	154	45
13,500 hrs. 920° F oil outlet	0.06	85,430	38,490	44.0	42.0	152	73
3,600 hrs. 1,200-1,300° F tube tem.	0.09	84,690	42,050	26.0	26.0	145	59
10,000 hrs. pre-heater tube	0.20	92,700	73,900	16.0	9.0	285	22

(From Symposium on Effect of Temperature on the properties of Metals. A. S. T. M. p. 339. Data attributed to H. D. Newell).

Furthermore the decomposition affected the mechanical properties as indicated in Table I and Table II.

With these various phenomena in mind, it was decided to study the magnetic, microscopic and corrosion behaviors of a number of alloys.

II. Alloys Examined and the Method of Procedure

The alloys which were used in this work had the analyses shown in Table III. All of these steels were supplied in the hot-rolled condition, except alloys 18-8-1, X, Y, and S. The treatment which these alloys received depended on the nature of the investigation. Some of them were put through a process of "homogenizing," which consisted in heating at elevated temperatures (1900 to 2000 degrees Fahr.) for a relatively long period of time, while others were investigated without such preliminary treatment: the reason back of it being the desire to ascertain whether the constitutional characteristics of steels in "as-rolled" condition have any influence on the behavior of steels at the temperatures of decomposition. Since, however, the hot-rolled condition may vary considerably, and since the structural constituents of steels under investigation are but little affected by short time heating at moderate temperatures, but decidedly so at higher temperature, the samples for this part of the investigation have received a quenching treatment at temperatures ranging from 1600 to 2400 degrees Fahr. Incidentally, it also seemed of much interest to learn what effect, if any, the recommended quenching (from 2100 degrees Fahr.) has on decomposition. Following quenching, the alloys were subjected to heating for periods of 100 and 250 hours within the temperature range of decomposition. The selected temperatures were 1100, 1200, 1400, 1600 degrees Fahr.

As has already been stated, the progress of decomposition was judged by means of magnetic analysis, by means of the corrosion test in copper sulphate plus sulphuric acid solution (unfortunately adopted as a standard test), and the corrosion in dilute hydrochloric acid and other acids, and by microscopic examination. Of these, the magnetic measurements required the most careful handling. A routine method was adopted, which was essentially as follows: after bars of suitable length were cut, they were subjected to careful machining, after which the cold-worked material on the surface was removed by deep etching. Once deep etched, these samples never

Table III

Chemical Compositions of Alloys Examined

Alloy	Carbon	Cr	Ni	Co	Si	Cu	Mo	Mn
18-8-1	0.010	19.11	8.85		very low			very low
18-8-4	0.046	18.78	8.88					
18-8-6	0.058	19.22	8.59		0.268			0.58
18-8-13	0.13	18.50	8.50		0.40			0.60
18-8-22	0.22	18.73	8.67		0.38			0.64
R	0.106	12.16	12.21		0.27			0.39
S	0.010	26.65	21.34		very low			very low
P	0.146	18.52	9.50	2.20	0.52			0.67
U	0.11	19.87	10.23		0.25	1.15	0.85	0.27
H	0.13	18.88	9.31		0.48	1.67	1.55	0.64
Q	0.26	18.00	8.00		2.08			
A	0.18	17.07	8.00				1.00	
B	0.21	17.34	8.00				1.68	
C	0.21	17.44	8.00				2.85	
D	0.18	15.95	8.00			1.20	0.04	
E	0.21	17.85	8.00			2.26	0.09	
F	0.20	15.80	8.00			3.20	0.03	
UU	0.19	18.21	9.06			1.02	0.97	
G	0.20	17.34	8.00			1.01	0.90	
N	0.19	15.80	8.17			0.88	1.97	
O	0.21	18.19	8.00		0.35	1.76	1.03	0.37
L	0.21	18.36	8.17		0.36	1.78	2.17	0.42
M	0.23	17.20	8.00		0.31	2.72	3.08	0.69
X	0.20	22.00	11.00					
Y	0.19	18.32	12.02					

received any treatment, such as stamping for example, which might have affected their magnetic characteristics. The next step was to obtain magnetic readings. First we secured the magnetic characteristics of each sample that was to be subjected to decomposition. After a while, however, this practice was discontinued, since we observed practically no variation from sample to sample similarly treated. Usually the amount of the magnetic phase is very small as can readily be seen from the curves, which follow, and which show the magnetic conditions in "as quenched" samples.

The decomposition treatment then followed. If a very thin oxide film was observed, as was sometimes the case, then the samples were deep etched again, washed in water, dried in alcohol, and again investigated magnetically. For magnetic measurements we were able to use a modified Fahy permeameter.

III. Experimental Results

The first series of experiments (Fig. 6) dealt with the influence of carbon content on decomposition. Four of the alloys, namely, those with 0.046, 0.058, 0.13 and 0.22 per cent carbon, were commercial alloys. The fifth one, however, containing 0.010 per cent carbon, was prepared from electrolytic iron, chromium, and nickel, the last two

containing only minute amounts of carbon. Melting was done in an induction furnace under an atmosphere of argon. Certain peculiarities of this alloy will be described later.

That the decomposition treatment results in the formation of a magnetic phase was pointed out in a previous publication[3]. In that investigation, however, the alloys studied contained appreciable amounts of carbon, from 0.12 per cent up, far in excess of carbon

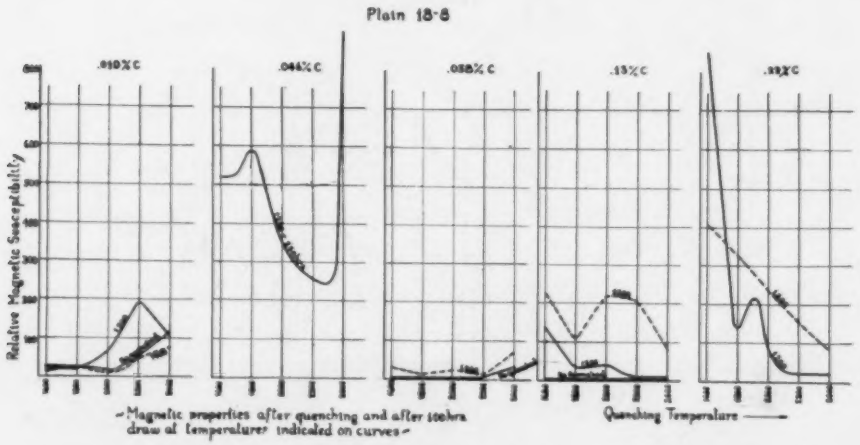


Fig. 6—Magnetic Properties of Plain 18-8 Alloy After Quenching and After 100 Hours Draw at Temperatures Indicated.

solubility in austenite at room or even elevated temperatures[4]. Consequently, when dealing with alloys of extremely low carbon content (such as 0.01 or 0.046 per cent) we must keep the figures for solubility in mind and interpret the magnetic curves in terms of the constitutional diagram, otherwise contradictory observations will be noted with consequences of erroneous conclusions. In this connection the diagram (Fig. 27), reproduced from the work of Bain and Aborn[3] and corrected in accordance with present findings, will be of much help in the correct interpretation of magnetic curves.

From the curves (Fig. 6) we observe at once that the amount of relative magnetic susceptibility is at a decided minimum at about 0.06 per cent carbon. A rapid increase in magnetic susceptibility is brought about either by raising or lowering carbon content. This is evident from a comparison of the 1200 degrees Fahr. decomposition curve for an alloy containing 0.058 per cent carbon with similar curves

[4]According to Strauss the solubility of carbon in 18-8 alloy is at least 0.04 per cent at 600 degrees Cent., while Bain and Aborn suggest "a slightly lower solubility." The present authors have reason for believing that the figure as given by Strauss is probably correct: but the solubility at room temperature still remains a conjecture.

for alloys of 0.01, 0.046 and 0.13 per cent carbon. The causes underlying the change in magnetic characteristics are inherently different. In one case when raising the carbon content we observe the evidence of decomposition; i. e., precipitation of carbides and accompanying phase change. In another case when the carbon content of the alloy is lowered (as, for example, down to 0.01 per cent carbon), no carbide precipitation can be detected by most careful microscopic observations. This is exactly what could have been predicted, because in such alloys we do not need carbide precipitation for the presence of magnetic material. Their strong magnetism is due to the coexistence of two phases, one magnetic and another nonmagnetic, as is depicted in Fig. 27. The microscopic study of this particular alloy (exact composition being carbon 0.010 per cent, chromium 19.11 per cent, nickel 8.85 per cent) proved to be exceedingly interesting. From among several samples we have chosen the one that was quenched from 2100 degrees Fahr. and then maintained at 1200 degrees Fahr. for one hundred hours. Its magnetism after the temper was more than five times that after the quench. Its structure is shown in Figs. 7 and 8. The sample does not consist of polyhedral grains, separated one from another by the products of decomposition, as would be the case had the carbon content been higher, Figs. 9 and 10. No trace of decomposition at grain boundaries is found. But the grains themselves have undergone partial transformation from gamma to alpha, giving the appearance of, whatever we may choose to call it, martensite-like or Widmanstätten-like structure. In other words, magnetic phase is not confined to grain boundaries. Furthermore, its composition (as regards chromium and nickel) should not be any different from that of nonmagnetic austenite. Bearing in mind that the mere presence of ferritic phase is not, necessarily, a criterion of corrodibility (as is so well exemplified by common stainless steels), we should hardly expect 0.01 per cent carbon 18-8 alloy to act toward corrosive media in the same way as would alloys with higher carbon. This was well borne out by subsequent tests. Hence while the difference in relative magnetic susceptibility means a certain readjustment of phases (with the tendency to approach an equilibrium), the corrodibility proper depends upon several factors, among which the most important ones are probably (a) the composition of the magnetic phase, (b) the distribution of phases, (c) lattice distortion, and (d) quite a variable term "passivity." In other words, the magnetic characteristics of the plain chromium-nickel alloys, with-

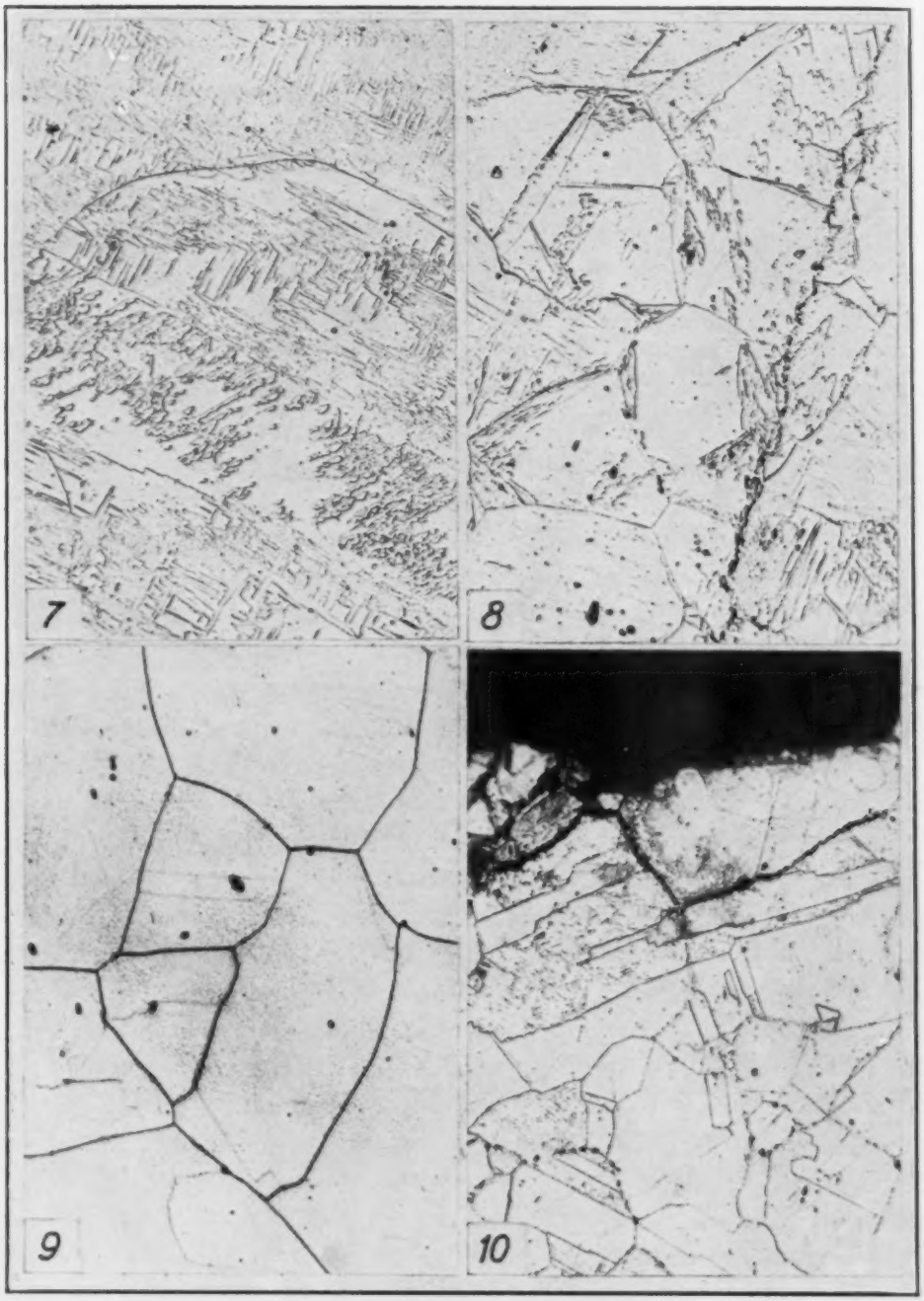


Fig. 7—Alloy No. 18-8-1 Quenched from 2200 Degrees Fahr., Heated to 1200 Degrees Fahr. for 100 Hours. Etched With Aqua Regia. × 250.

Fig. 8—Alloy No. 18-8-1. Same as Fig. 7. Another Typical Spot.

Fig. 9—Alloy No. 18-8-13 Badly Decomposed. Etched With Murakami Reagent. × 250.

Fig. 10—Commercial 18-8 Alloy Badly Decomposed. Note Start of Intergranular Corrosion. Etched with Murakami Reagent. × 250.



1200

agent.

nular

Table IV
Results of Magnetic Determinations and Corrosion Tests

Magnetic Characteristics								Corrosion Characteristics					
Alloy No.	18-8-22	18-8-13	18-8-6	18-8-1	S	R	Treatment °F.	Alloy No.	18-8 -22	18-8 -13	18-8 -6	18-8 -1	S	R
Carbon Per Cent	0.22	0.13	0.058	0.01	0.01	0.11	Quench. Decomp.	Carbon Per Cent	.22	.13	.058	.01	.01	0.11
	1.20	1.69	1.83	27.5			1600		N	N	N			
	1.17	1.53	1.45	16.8			2000		N	N	N			
	1.13	1.89	34.6	113.2			2400		N	N	N			
	39.0	45.4	18.8				1600 1100		HA	A	A			
	29.0	10.1	7.90				1800 1100		HA	A	HA			
	3.0	2.9	2.26				2000 1100		SA	SA	SA			
	2.80	9.2	6.98				2200 1100		HA	A	HA			
	1.50	2.2	33.3				2400 1100		HA	HA	A			
		33.2		23.5		72.8	1600 1200		A	A	A	N		SA
				20.3		30.2	1800					N		
				63.0		3.1	2000		A	A	HA	N		A
				194.0		20.3	2200					N		
				103.0		18.6	2400		A	A	A	SA		SA
	405.0	229.0	30.6	14.4	0.37	225.0	1600 1400		HA	HA	HA	N	N	SA
	329.0	110.0	15.2	28.6	0.37	212.0	1800		HA	HA	HA	N	N	
	239.0	220.0	23.6	13.7	1.01	119.0	2000		A	SA	SA	N	N	SA
	153.0	204.0	16.2	50.0	0.65	59.0	2200		HA	HA	HA	N	N	
	87.0	82.0	75.8	78.3	0.00	36.7	2400		A	A	HA	N	N	SA
	77.4	8.50	1.99				1600 1600		A	HA	N			
	77.3	13.50	2.08				1800		HA	HA	N			
	184.0	86.40	3.11				2000							
	28.3	28.80	1.99				2200		A	HA	HA			
	46.6	102.0	37.90				2400		HA	HA	A			

VHA (very heavy attack) means penetration (disintegration) more than 0.15 inch.
HA (heavy attack) means penetration (disintegration) from 0.09 to 0.15 inch.
A (attacked) means penetration (disintegration) from 0.04 to 0.08 inch.
SA (slight attack) means penetration (disintegration) less than 0.04 inch.
N (no interganular corrosion).

out additions of other elements, are not to be taken as the measure of their corrodibility, regardless of their carbon content. However, in alloys with carbon content higher than a certain amount such magnetic characteristics do serve as an estimate of the extent of decomposition. The latter may or may not cause the corrodibility, depending primarily on the composition of the alloys (i. e., whether any special additions were made) with the consequence that each class of alloys must be considered separately.

Table IV shows the results of magnetic determinations and actual corrosion tests, as conducted on samples of 18-8 with variable carbon content. The samples used for corrosion tests were parts of the samples subjected to magnetic measurements. For corroding media "standard" copper sulphate and sulphuric acid solution, nearly boiling was used. The duration of test was 100 hours. For the sake of brevity this test will be spoken of as "sulphate test." It was found impractical to measure the corrodibility by what may be called "qualitative" terminology, rather than by the quantitative measurements. For convenience in interpretation of data let us divide alloys of 18-8 type into two groups, one with carbon content very low (0.01 and perhaps up to 0.03 per cent), and another with carbon between 0.06 and 0.22 per cent. Alloys belonging to the first group are not subjected to corrosion, regardless of their previous treatment. Whether air-cooled, quenched, quenched and tempered at 1200, 1400 degress Fahr., etc., although quite magnetic, they remain remarkably immune to corrosive action of the drastic test, thus fully upholding the previously expressed belief. In these alloys it is simply a case of the magnetic phase remaining non-corrosive due to the same concentration of chromium and nickel in both magnetic and non-magnetic phases. It is quite possible that by a certain treatment alloys of this type might be fully converted into the ferritic state, and yet their corrosion resistance would not suffer. Consequently, when drawing a parallel between corrosion resistance and relative magnetic susceptibility, this group of alloys must be regarded as an exception. The detailed study of their magnetic characteristics shows that these change with the change in treatment.

It is not so easy, however, to draw definite conclusions from the results on alloys in Group II. The reasons for this difficulty are obvious. Alloys with carbon above 0.06 per cent (this figure is, of necessity, quite approximate) do not show the coexistence of magnetic and nonmagnetic phases at any temperature save in close

proximity to transition point. Hence, the sudden appearance of the magnetic phase can be due only to the precipitation of carbides or, in other words, due to the local change in composition; perhaps a better expression would be difference rather than change. This difference may be quite great and again it may not, for while the process of decomposition goes on, two tendencies manifest themselves. One is the separation of carbides, accompanied by the impoverishment of the neighboring material. The other is migration of chromium, nickel, and probably carbon from richer parts into those impoverished. The total effect will be dependent upon these tendencies, and so will the corrosive properties. However, it will be seen from the table that, invariably, there is a definite relationship between relative magnetic susceptibility and the tendency for corrosion. At a given temperature of decomposition the total effect of diffusion is never sufficient to restore the original composition to an extent such as to make the change from ferrite back into austenite possible at the given temperature. Neither, apparently, is it ever sufficient to prevent intergranular corrosion.

There is not, and could hardly be expected to be, a precise, numerical relationship. If the relative magnetic susceptibility and the relative corrosion resistance are each plotted against the composition of magnetic phase, the curves so derived cannot be expected to be of the same general appearance. If the relative magnetic susceptibility is close to one[5], the sample, regardless of the treatment it has undergone, is certain to remain untouched by corrosive action of sulphate solution. In the case of 18-8 at the lower end of the carbon range in Group II this figure can be somewhat higher.

It does not require much increase in decomposition as indicated by these relative figures for magnetic susceptibility to cause the samples to be unsuitable from the point of view of the sulphate test. Unfortunately, it means that although the composition of the impoverished material may be just a little off that of the parent alloy, yet this small difference is sufficient to cause destructive corrosion. In other words, alloys of this type are extremely sensitive and even a slight disturbance of their chemical homogeneity is apt to result in much diminished fitness for some applications of these alloys.

It also appears that mere lowering of carbon content (to the values commercially possible) does not render 18-8 alloys immune

[5]As shall be seen, the values of relative magnetic susceptibility can serve as a basis for calculating the actual amounts of magnetic phase present in a sample.

to destructive decomposition: whether we have 0.06 per cent carbon or as high as 0.34 per cent carbon, these alloys, and others with carbon content within this range will decompose[6]. In order to prevent decomposition we would have to go as low as 0.02 to 0.03 per cent carbon which is obviously quite impossible commercially.

In the course of this extended investigation, during which more than 500 samples were tested and studied, it was repeatedly noted that the lower the carbon content the lower was the upper temperature at which decomposition ceased. For example, the temperature of 1600 degrees Fahr. seems to be quite safe for an alloy with 0.06 per cent carbon, at least heating at that temperature for 250 and 900 hours did not impair its resistance to corrosion. It is seriously doubted if increasing the number of hours would have an appreciable effect. This is indicated by the data of Table II. On the other hand, for alloys with higher carbon (the next one investigated had 0.11 per cent carbon) the temperature of 1600 degrees Fahr. is still dangerous. The higher the carbon content, the more pronounced and the more easily induced is the decomposition. Whether the length of decomposition period has any appreciable influence is being investigated.

IV. Iron-Chromium-Nickel Diagram and Magnetic Measurements

To the best of our knowledge, an alloy with carbon as low as 0.01 per cent has been investigated for the first time[7]. It appears that rather interesting information in regard to the constitutional diagram for iron-chromium-nickel alloys (Fig. 27) can be derived from the study of magnetic curves (Fig. 6). It is believed that carbon content of 0.01 per cent could be regarded as being negligible[8] and that alloy considered as an iron-chromium-nickel alloy.

Quenching from gradually increasing temperatures shows small amounts of the magnetic phase. Theoretically, no magnetic phase should exist at 1600, 1800 or 2000 degrees Fahr. since the alloy is in

[6]That is, as far as the decomposition can be detected: whether decomposition of low carbon 18-8 is as dangerous as is universally held will be taken up later.

[7]Aborn and Bain report an alloy with "about 0.02 per cent."—Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 859.

[8]Maybe contaminated Pittsburgh air had something to do with this figure of 0.01 per cent; the calculations based on composition of charge show only 0.003 per cent carbon could be present.

the gamma field. The very small amount of magnetism found could hardly be considered a discrepancy. The increase in magnetism on quenching from 2200 degrees Fahr. is so notable that apparently a zone of alpha and gamma phases has been entered, the relative amounts of which change with increasing temperatures. In conse-

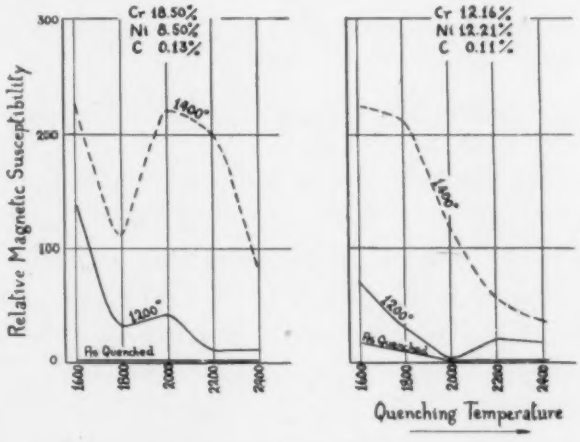


Fig. 11—Comparison of Relative Magnetic Susceptibility Between 18-8 Alloy and 12-12 Alloy.

quence, the slope of the line separating the austenitic field from the field of austenite and ferrite will have to be changed to that shown by the dotted line.

This alloy was reheated to two temperatures, namely 1400 and 1200 degrees Fahr. The intersection of coordinates, one representing composition and the other 1400 degrees Fahr., brings us in the field of gamma iron. Maintaining the alloy at this temperature should be accompanied by the disappearance of ferrite (alpha iron) and consequent decrease in magnetic values. The magnetic curve for 1400 degrees Fahr. indeed shows a tendency in this direction, but a somewhat prolonged time of heating would be required to result in the complete disappearance of the magnetic ferritic phase.

On the other hand, maintaining the alloy at 1200 degrees Fahr. brings it into the "ferrite-austenite" field with the subsequent readjustment of coexisting phases. Nonmagnetic austenite retained on quenching from various temperatures is partly converted into magnetic ferrite. The 1200 degrees Fahr. temperature curve clearly shows such to be the case; why, however, the same alloy quenched from 1600, 1800, and even 1900 degrees Fahr. does not show phase change remains to be explained. Probably some unforeseen and un-

detectable error has crept in, since a 0.046 per cent carbon alloy (Fig. 6) is in perfect accord with the line of reasoning. It is rather worthy of attention that high temperature quenching, sufficiently high to start the peritectic reaction, shows a most pronounced unstability of austenite formed as a result of such reaction. This observation is probably of interest only to the student of physical chemistry and may, some time, be made a subject for a separate paper.

V. Decomposition vs. Chromium and Nickel Content

In addition to the 18-8 type a series of alloys was prepared containing various amounts of chromium and nickel. Although it was intended to cover in this work a number of alloys with chromium from 12 to 30 per cent, nickel from 4 to 20 per cent and carbon from 0.01 to 0.15 per cent, it was impossible to have all the results classified and studied before this paper goes into print. Obvious interest displayed by several members of the Society in regard to merits of alloys varying in chromium and nickel contents seemed to justify a short account.

Five alloys were investigated:

		Desired Analysis Per Cent			Actual Analysis Per Cent		
		Carbon	Chromium	Nickel	Carbon	Chro-mium	Nickel
Alloy	12-12-1	0.01	12.00	12.00	....	....	....
Alloy	R	0.01-0.15	12.00	12.00	0.11	12.16	12.21
Alloy	S	0.01	25.00	20.00	0.01	26.65	21.34
Alloy	X	0.15-0.20	25.00	20.00	0.20	22.00	11.00
Alloy	Y	0.15-0.20	18.00	12.00	0.19	18.32	12.02

The first two alloys are strictly within the composition that formed the topic of a lively discussion. The last three lie approximately within the limits of composition of some prominent iron-chromium-nickel commercial alloys.

Through a mistake, alloy 12-12-1 was lost and the writer was able to secure only a small piece which precluded the possibility of magnetic measurements but permitted metallographic studies. The remaining three alloys were carefully investigated.

Alloy R was subjected to quenching followed by heating to 1200 and 1400 degrees Fahr. and showed a definite decomposition. Relative magnetic susceptibility is greatly increased at both temperatures, and, in general, the alloy follows the rules outlined for 18-8 type of composition. The comparison, insofar as relative magnetic suscepti-

bility is concerned, between 18-8 and 12-12 is given in Fig. 11. When subjected to sulphate corrosion test it behaves like the rest of plain chromium-nickel alloys; i. e., it is readily attacked.

It appears, therefore, that partial substitution of chromium by nickel is not effective from the point of view of decomposition, corrosion, and destruction. When the composition of 18-8 is modified by increasing nickel to 12 per cent (with 0.19 per cent carbon), the resulting alloy is still subject to decomposition with its accompanying evils. The lower and upper limits of the decomposition range, however, may not coincide with those for 18-8 alloys, but the trend, the appearance, and the properties of the decomposed material are quite the same. It is also true that, apparently, a longer time for the decomposition process is required before the material is rendered definitely unsuited for further service. The importance of carbon content should not be overlooked.

Even when an alloy with 22 per cent chromium, 11 per cent nickel and 0.20 per cent carbon is subjected to decomposition, the results are exactly the same as in the case of 18-8. Again, what was said of 18-12, is also true of 22-11. The limits of decomposition range are shifted and decomposition does not set in nearly as readily as in 18-8 alloys, except under special circumstances such as, for example, severe deformation of the material.

On the other hand, a high chromium, high nickel alloy containing practically no carbon (chromium 26.65 per cent, nickel 21.34 per cent, carbon 0.01 per cent) behaves exactly like an 18-8 alloy with carbon just as low. It does not become magnetic after decomposition (Fig. 12) and is not affected by sulphate corrosion mixture. Its structure remains typically austenitic and the writer did not observe any changes with different heat treatment.

Only a few alloys designated to serve as guiding posts are here described. Full information on this general type of high chromium, high nickel alloys will, it is hoped, soon be available for general consideration.

VI. Decomposition of 18-8 Type Alloys with Additions of Special Elements

This series of experiments was made on alloys (of general 18-8 composition) to which were added different amounts of cobalt, copper, molybdenum, and silicon, singly and in combination. Other

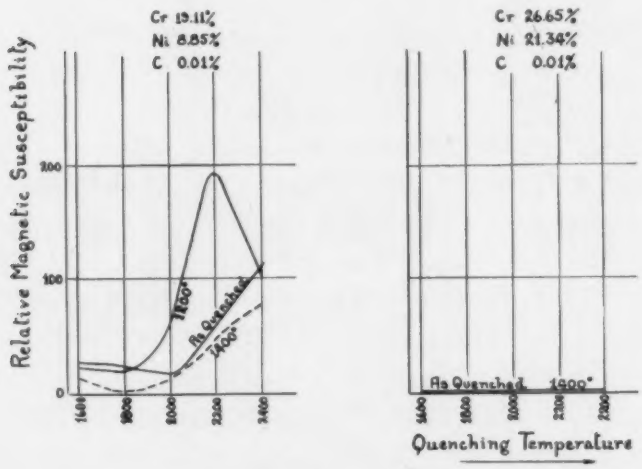


Fig. 12—Comparison of Relative Magnetic Susceptibility Between 19-9 and 27-22 Alloys.

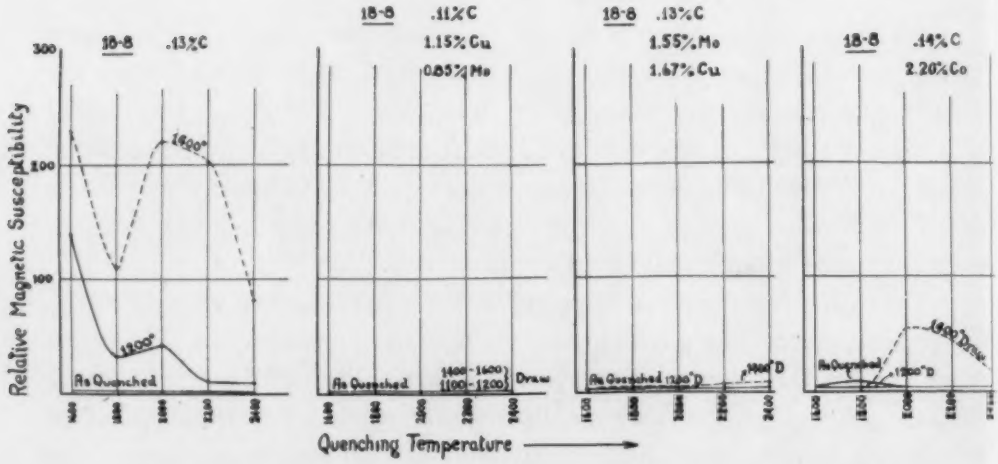


Fig. 13—Relative Magnetic Susceptibility Plotted Against Quenching Temperature on Plain 18-8 Alloys.

alloys containing manganese and tungsten, and their combination with cobalt, copper, molybdenum, titanium, and silicon are now in the process of investigation. A rough subdivision of the alloys according to their carbon content may be drawn as follows:

Group III.	Carbon 0.13 to 0.15 per cent
Group IV.	Carbon 0.20 to 0.22 per cent
Group V.	Carbon 0.05 to 0.10 per cent

Most unfortunately, some difficulties were experienced in preparing alloys of Group V and their investigation cannot be completed for some time.

It was shown above that neither lowering the carbon content (to the practical and commercially possible values), nor the readjustment of chromium and nickel contents within rather narrow limits, would produce that degree of security from decomposition as naturally would be demanded of these high priced alloys. It was repeatedly pointed out that the process of decomposition is the result of two distinctly physico-chemical phenomena, precipitation and phase change. Hence our efforts in combating such decomposition should be directed toward (a) increasing the solubility of carbides at all temperatures, (b) producing a matrix which would resist migration of carbides to the grain boundaries and their agglomeration, (c) producing a matrix which in itself (even if carbides have separated) would resist corrosion, (d) forming carbides of elements other than chromium, and (e) rendering the matrix less susceptible to a phase change.

Of these (a) and (b) are important, because of the decreased strength of decomposed alloys, and (c), (d), and (e) because of their lowered resistance to corrosion. Addition of special elements is a most natural thought. That such additions, provided they accomplish the purpose, justify the additional expense entailed can hardly be disputed.

In order to avoid any chance of a mistake and in order to be able to draw reliable conclusions, a series of four alloys (belonging to Group III) were treated simultaneously.

	Carbon	Chromium	Nickel	Molybdenum	Copper	Cobalt
Alloy 18-8-13	0.13	18.50	8.50			
Alloy U	0.11	19.87	10.23	0.85	1.15	
Alloy H	0.13	18.88	9.31	1.55	1.67	
Alloy P	0.14	18.52	9.50			2.20

The samples were quenched from 1600 to 2400 degrees Fahr. (at 200-degree Fahr. intervals) and tempered, some at 1100, 1200, 1400, and 1600 degrees Fahr., while others, due to the tremendousness of the undertaking, only at 1200 and 1400 degrees Fahr. These last two were selected primarily because plain 18-8 showed the worst condition when heated at these temperatures. The results of relative magnetic susceptibility plotted against quenching temperature (for each tempering range) are given in Fig. 13 and the detailed study of alloy U, in Fig. 14. It will be observed that the combination of copper and molybdenum practically eliminated the phase change, although microscopic examination of the samples shows the presence of decomposition at the grain boundaries. Whether molybdenum alone or

copper alone is as potent a factor (in alloys in which carbon is between 0.11 and 0.13 per cent) will soon be decided by an investigation which is well underway. Cobalt, however, seems to be much less effective. It shows marked increase in relative magnetic susceptibility, especially when subjected to decomposition at 1400 degrees Fahr. However, magnetic properties of cobalt make the deductions from

Table V
Results of Magnetic Determinations and Corrosion Tests

Alloy No.	Magnetic Characteristics 18-8-13	P	U	H	Corrosion Characteristics 18-8-13	P	U	H	Treatment Quench	Temper
			1.69			N	N	N	N	1600	None
			1.53			N	N	N	N	2000	None
			1.89			N	N	N	N	2400	None
			45.4			HA		HA		1600	1100
			10.1			A		A		1800	1100
			very low								
			2.9					SA		2000	1100
			very low								
			9.2			A				2200	1100
			2.2		1.29	HA		HA		2400	1100
			38.2	3.13	1.66	A	HA	HA	N	1600	1200
					0.90					1800	1200
				1.03	1.27	A	HA	A	N	2000	1200
					0.83					2200	1200
				1.84	1.22	A	A	A	N	2400	1200
			229.0	1.74	1.37	1.12	HA	SA	N	N	1600	1400
			110.0		1.29	0.93	HA				1800	1400
			220.0	58.0	1.61	2.90		A	SA	N	2000	1400
			204.0		1.62	9.70	HA				2200	1400
			82.0	16.3	4.82	9.30	HA	A	A	SA	2400	1400
			8.50		1.29		HA		N		1600	1600
			13.50		1.18		HA				1800	1600
			86.40		1.22				N		2000	1600
			28.80		0.96		HA				2200	1600
			102.0		1.19		HA		N		2400	1600

magnetic data rather questionable. From the magnetic data it was fully anticipated that the apparent suppression of phase change could greatly improve the corrodibility of such alloys, even under such drastic conditions as sulphate corrosion. Consequently, when the results of actual corrosion tests (Table IV) became available they were decidedly disappointing. However, they furnished a ground on which the reliability of sulphate test may well be argued. This, however, will be taken up later.

Referring to Table V (in which the notations are the same as in Table IV) we notice that, in spite of the suppression of the phase change, the corrosive action of copper sulphate and sulphuric acid has readily taken place, except in one or two cases. We also notice that there is, apparently, no relation between relative magnetic susceptibility and corrodibility; the cobalt-bearing 18-8 alloy is readily

attacked whether the figure for magnetism is high or low. The same is true of 18-8 with copper and molybdenum. Evidently then, even though the phase change is suppressed, decomposition through the separation of carbides (such decomposition readily observable under the microscope), so changed the composition in the adjacent areas, that the latter became easily corrodible. The action of added copper and molybdenum seems to act in the same way as decrease in carbon;

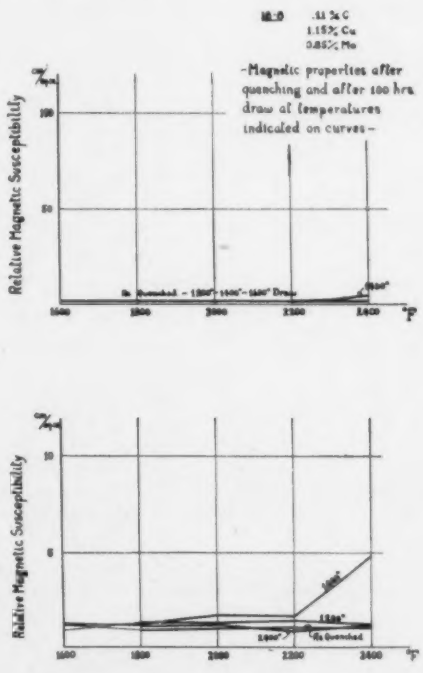


Fig. 14—Detailed Study of Alloy U Showing Magnetic Properties After Quenching and Drawing for 100 Hours.

the upper limit of decomposition temperature is lowered. Experiments, repeated several times, prove that decomposition at 1600 degrees Fahr. is practically negligible. With further increase in copper and molybdenum additions (up to 1 and ½ per cent each) the results become quite encouraging. At both temperatures, 1200 and 1400 degrees Fahr., harmful decomposition is practically suppressed, except when an alloy was quenched from a relatively high temperature (2400 degrees Fahr.). This is an entirely different matter, already referred to by the writer in this and in previous publications.

From the considerations of a vast amount of data, gathered during the present investigation, the writer came to the conclusion

that for a certain carbon content there is a corresponding amount of added special elements, the amount dependent solely on the nature of the element, which would render 18-8 immune to decomposition, deterioration, and corrosion, providing these added special elements act in accordance with five stipulations laid out previously. One of the future problems would be to ascertain the relative power of different special elements. Cobalt and silicon, for example, appear less desirable than either copper or molybdenum, while others may

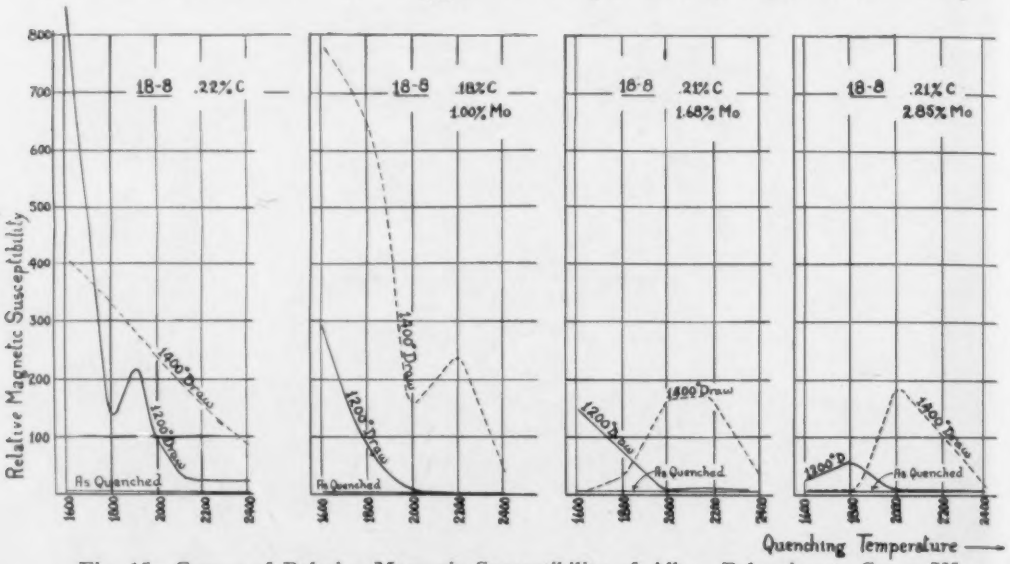


Fig. 15—Curves of Relative Magnetic Susceptibility of Alloys Belonging to Group IV—Table VI.

prove to be more powerful. We do not have, as yet, sufficient data to judge the relative merits of copper and molybdenum. It seems that with about 2 per cent copper and molybdenum (total) the alloy is decidedly improved. A private communication to the writer states that 18-8 alloy with 3 per cent molybdenum resists sulphate corrosion to a remarkable degree.

In the Table VI are recorded the results on alloys belonging to Group IV. A much larger number of alloys was studied. Presumably due to high carbon content the results are not on the whole very encouraging and are rather difficult to interpret. The magnetic characteristics of these alloys are reproduced in Figs. 15, 16, 17 and 18, while their relative corrodibility is indicated in Table VI.

The general conclusions may be summarized as follows:

(a) Additions of copper up to 3.20 per cent do not help decomposition and do not prevent phase change.

Table VI

Magnetic and Corrosion Characteristics of Alloys of Group IV

Alloy No.	18-8 -22	Q	A	B	C	D	E	F	UU	G	N	O	L	M	Treatment Quench	Treatment Temper
	N	....	....	....	....	....	....	....	....	....	....	....	....	....	1600	....
	4.2	....	....	....	....	....	....	....	....	....	....	....	....	....	2000	....
	N	....	....	....	....	....	....	....	....	....	....	....	....	....	2400	....
	1.17	....	....	....	....	....	....	....	....	....	....	....	....	....	1600	1100
	N	....	....	....	....	....	....	....	....	....	....	....	....	....	1800	1100
	1.13	....	....	....	....	....	....	....	A	....	....	....	....	....		
	A	....	....	....	....	....	....	....	0.7	....	....	....	....	....	2000	1100
	59.0	....	....	....	....	....	....	....	....	....	....	....	....	....	2200	1100
	A								A							
	29.0	....	....	....	....	....	....	....	1.84	....	....	....	....	....	2400	1100
	A									A	SA	N	N	N		
	3.0	....	....	....	....	....	....	....	....	201	78.3	103	1.98	4.75	1600	1200
	A														1800	1200
	1.50	....	....	....	....	....	....	....	....	....	....	....	....	....		
	A	....	A	SA	A	SA	SA	SA	....	SA	A	A	A	A		
	....	A	A	SA	27.4	SA	115	144.5	....	2.3	1.75	20.2	4.66	6.6	2000	1200
	A	13.8	299	148	N	238	A	HA	....	....	....	....	....	....	2200	1200
	....	HA	A	SA	N	A	A	HA		HA	VHA	VHA	HA	A		
	....	9.18	2.8	1.8	0.71	2.85	3.63	4.8	....	1.0	1.43	4.3	4.1	4.9	2400	1200
	A	A	HA	HA	VHA	HA	HA	HA	....	N	N	N	N	N		
	....	2.2	2.7	1.9	0.85	2.48	2.15	3.5	....	6.6	0.98	59.2	1.15	4.6	1600	1400
	HA	N	N	N	N	A	SA	SA	N							
	....	3.1	187	4.00	3.6	870	379	65	1.63	....	....	....	....	....	1800	1400
	....	SA	SA	SA	A	A	SA	HA	SA	SA	SA	SA	N	N		
	....	9.4	161	165	181	125	217	125	300	189	171	152	1.53	38.6	2000	1400
	....	HA	A	A	A	A	A	HA					N			
	....	5.4	43	35.3	15.5	25.3	22.5	18	....	....	....	....	48.5	....	2200	1400
		A							VHA	HA	A	A	N	N		
	....	77	....	....	....	....	....	....	127	19.4	37.6	76	2.0	9.4	2400	1400
		A							....	....	....	....	....	....	1600	1600
	....	77	....	....	....	....	....	....	....	....	....	....	....	....	1800	1600
		A							....	....	....	....	....	....	2000	1600
	....	28	....	....	....	....	....	....	....	....	....	....	....	....	2200	1600
		A							SA							
	....	46.6	....	....	....	....	....	....	7.8	....	....	....	....	....	2400	1600

In this table, A, SA, etc., have the same meaning as in previous tables.
Figures which follow the letters indicate relative magnetic susceptibility.

(b) Additions of molybdenum up to approximately 3 per cent do not suppress decomposition and do not prevent phase change.

(c) Additions of copper and molybdenum, providing their combined amount is approximately 4 per cent, do prevent phase

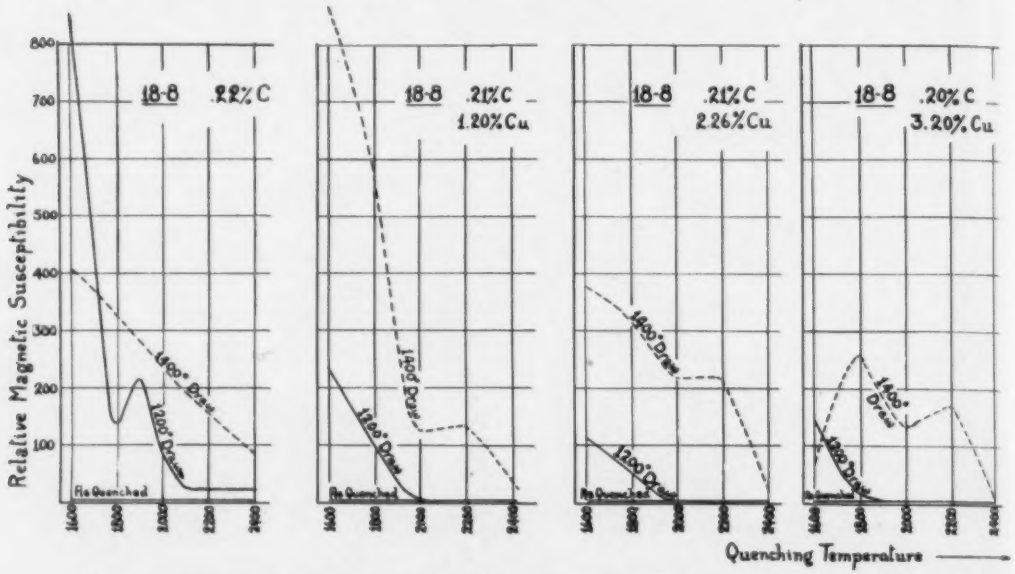


Fig. 16—Curves of Relative Magnetic Susceptibility of Alloys Belonging to Group IV —Table VI.

change but judging by sulphate corrosion tests and microscopic observations do not prevent decomposition.

(d) There is no relation between magnetic characteristics of the alloys and their corrosive properties in sulphate solution.

(e) The greater the amount of special additions, the lower is the upper limit of decomposition range.

(f) The addition of either copper or molybdenum alone, or both together decidedly improves the corrosive properties of plain 18-8 of similar carbon content. It is anxiously desired that the writer should not be misunderstood: the alloys, the characteristics and properties of which were just summarized, contained more carbon than we would normally anticipate using (except in special cases). The whole purpose of this part of the investigation was to ascertain whether we could or could not combat the evil influence of higher carbon by corresponding increases in additional elements, and if we could, how much of the additional element will be necessary. So far, we have investigated molybdenum, copper, and silicon. Others (manganese, tungsten, titanium, tellurium and their combinations) are being studied.

Such an attempt is perfectly justified by the decided improvements in the mechanical properties of some of the alloys made with special additions. These improvements concern not only room tem-

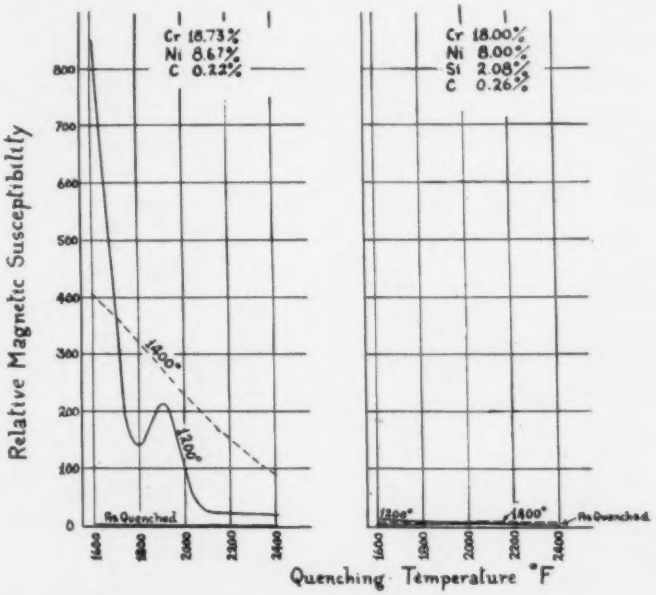


Fig. 17—Curves of Relative Magnetic Susceptibility of Alloys Belonging to Group IV—Table VI.

perature tests, but what is infinitely more important, tests at elevated temperatures. This subject will be dealt with in a separate publication.

VII. The Copper Sulphate Test

It will be remembered that in all previous discussions whenever "corrodibility" or "corrosion test" was referred to, it meant intergranular corrosion by the solution of copper sulphate and sulphuric acid, heated to boiling temperature and applied either for 24 hours (standard test) or 50 hours (in order to get better developed characteristics). And it will also be remembered that in most cases this test produced negative results, that is, the solution would attack the steel intergranularly, without much regard as to whether the decomposition was small or pronounced. In other words it is a powerful corroding agent, and the test is, in a way, a drastic one.

It appeared desirable to supplement the copper sulphate test with some other, known to be less drastic, and therefore more likely to be a check on the amount of decomposition. Also, one which

will give some idea concerning the relationship between decomposition and mechanical properties.

Corrosion of 18-8 alloys by different dilute acids has been investigated many times. In the laboratories of the Carnegie Institute of Technology an investigation was carried on in an attempt to secure information in regard to the relation between internal stresses of different types of 18-8 and corrodibility in different media.[9] It

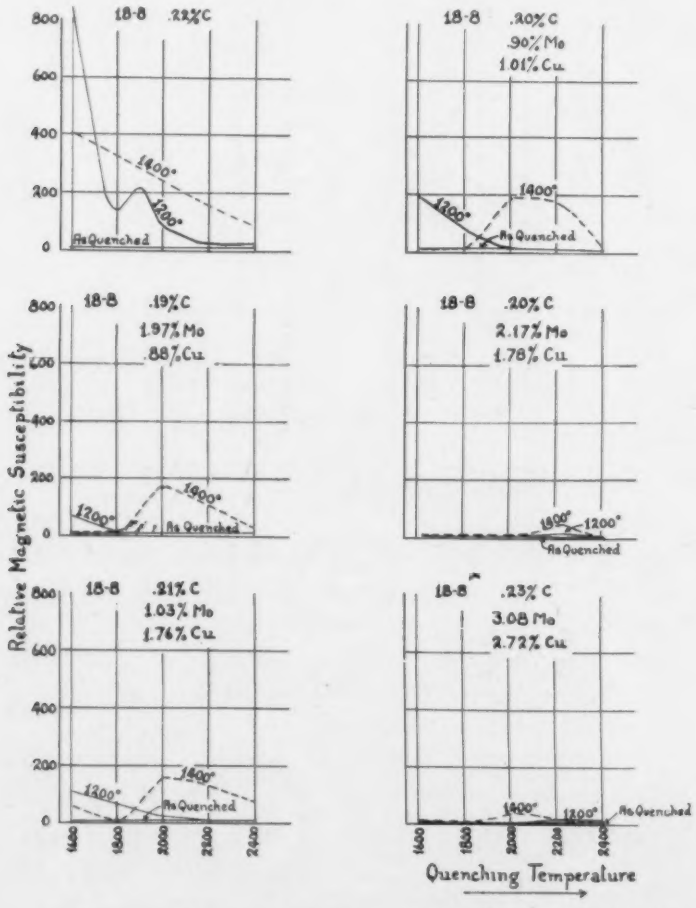


Fig. 18—Curves of Relative Magnetic Susceptibility of Alloys Belonging to Group IV—Table VI.

was found during the investigation that dilute hydrochloric acid (10 per cent) was yielding consistent and satisfactory results. Consequently a series of tests was made in which 18-8 alloys of different carbon contents and in different states of decomposition (as was judged by magnetic and microscopic analysis) were subjected to cor-

[9]André Hone. Master's Thesis. Library, Carnegie Institute of Technology.

rosion with 10 per cent hydrochloric acid at room temperature, observing all the precautions necessary for accurate corrosion work (i. e., as accurate as controllable factors would permit). To the same

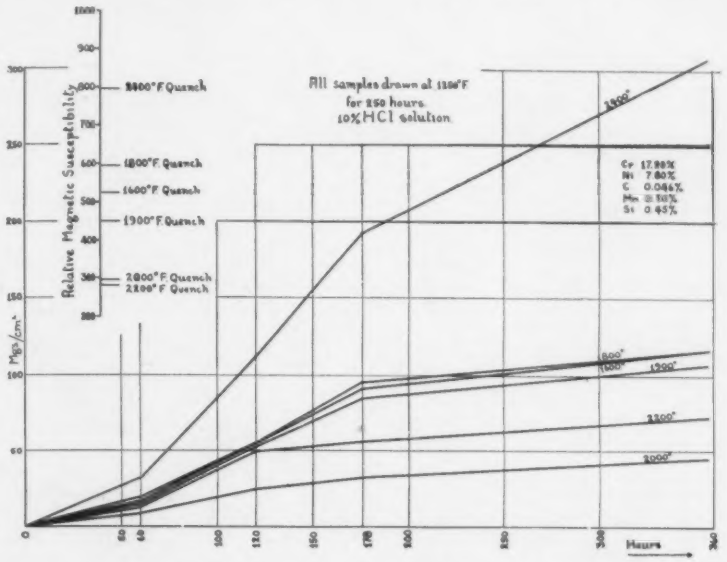


Fig. 19—Corrosion Rate of 18-8 Alloy in 10 Per Cent Hydrochloric Acid Solution.

test was also subjected a steel containing copper and molybdenum[10].

The composition of steels investigated was as follows:

Steel No.	Carbon	Chromium	Nickel	Copper	Molybdenum
18-8-4	0.046	17.2	7.8		
18-8-14	0.14	18.38	8.57		
18-8-23	0.23	17.96	7.95		
18-8-34	0.34	17.56	8.10		
U	0.11	19.87	10.23	1.15	0.85

Corrosion rate was many times less than in copper sulphate and it was found convenient to judge it by loss in weight per unit area (milligrams per square centimeter) and to plot the obtained values against time of immersion (hours). The samples were the same as those used for magnetic work. They were treated (quenched) at different temperatures and subjected to decomposition at 1200 degrees Fahr. for 250 hours. The results are plotted in Figs. 19, 20, 21 and 22, which, in addition to corrosion data, contain the figures for relative magnetic susceptibility, replotted from magnetic curves.

The agreement between the magnetic and corrosion data is

[10]G. C. Towner, U. S. N., A. C. Murdough, U. S. N., and E. A. Krockenberger, in writer's laboratory.

quite remarkable. The more magnetic the sample, the more readily it is attacked by the 10 per cent hydrochloric acid solution: this holds true for 0.046, 0.14, 0.23 per cent carbon content. In case of steel with 0.34 per cent carbon a discrepancy is found only at one of several

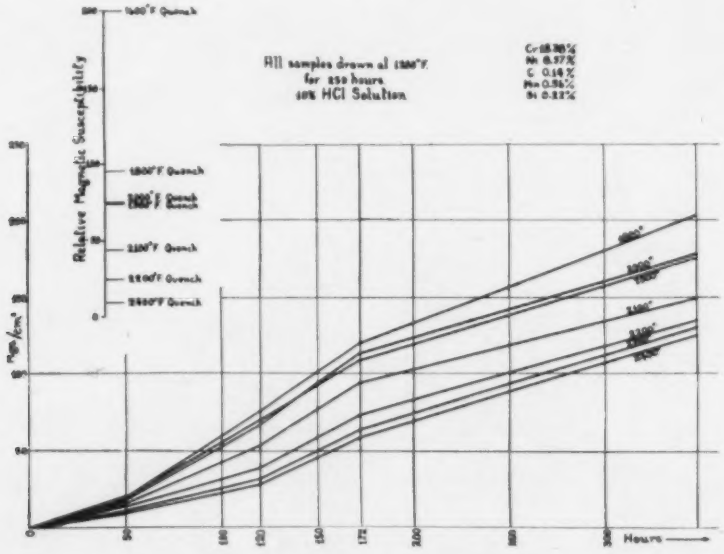


Fig. 20—Corrosion Rate of 18-8 Alloy in 10 Per Cent Hydrochloric Acid Solution.

quenching temperatures and this anomaly is easily explainable in an alloy of such high carbon.

The corrosion proper, in addition to its general action, appears to be somewhat intergranular in character, rather similar to copper sulphate. It is much more easily discerned because of the comparatively mild destructive action of dilute hydrochloric acid.

Fig. 23 represents similar results for an 18-8 alloy containing additional elements (1.15 per cent copper and 0.85 per cent molybdenum and 0.12 per cent carbon). We did not have an alloy of exactly the same analysis for magnetic testing, but another, close in composition, was so tested. The results are given in Fig. 23. The steel is practically nonmagnetic after attempted decomposition at various temperatures. It is also noncorrodible by 10 per cent hydrochloric acid, or at the most corroded so little as to consider such corrosion quite negligible especially when compared with plain 18-8. Yet, it is decidedly attacked by copper sulphate, and on the strength of its performance in sulphate bath would be adjudged useless. There can hardly be any doubt that 18-8 alloys of other varieties (that is with

addition of other element, or elements, subjected to limitations as set forth previously) would act the same way. It could, probably, be predicted that other corroding media, similar to dilute hydrochloric acid, would act in the same manner. It certainly is true of sulphuric acid. And so we are confronted with rather an interesting and perplexing argument. Of course, it may be entertained that after all,

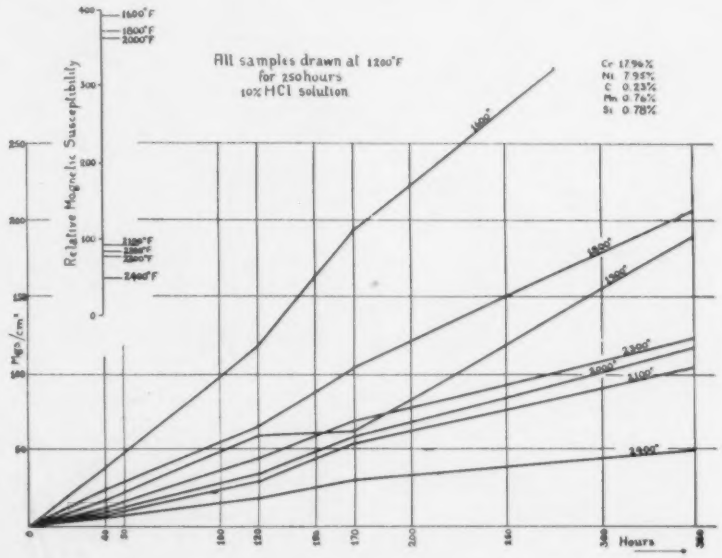


Fig. 21—Corrosion Rate of 18-8 Alloy in 10 Per Cent Hydrochloric Acid Solution.

wet corrosion, such as described, is not indicative of the properties of the material and that other data, for example, gas corrosion, or mechanical properties would throw more light on this question. True enough, during the last few months, a fairly large amount of data on corrosion of 18-8 by different gases, and under different conditions of temperature and static load, was collected. The experiments were conducted in such a way that a sample under investigation remained for some time in a furnace with well established temperature gradient. This gradient was between 1500 and 700 degrees Fahr. The duration of the experiment was at times as long as 100 hours and even 300 hours, certainly quite sufficient to induce decomposition on those parts of the samples which were maintained at the temperatures that lie within the limits of decomposition. The studies on steels of the compositions just mentioned are completed while others[11] are still under investigation. Noting the position of the break it was

[11] 18-8 alloys with W, Mo, Mo-Co, Mo-Cu-Co, Mn, Mn-Co.

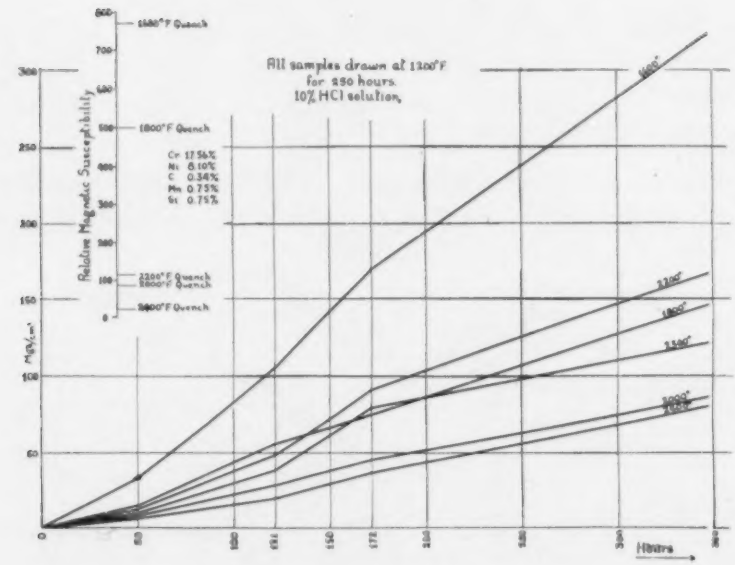


Fig. 22—Corrosion Rate of 18-8 Alloy in 10 Per Cent Hydrochloric Acid Solution.

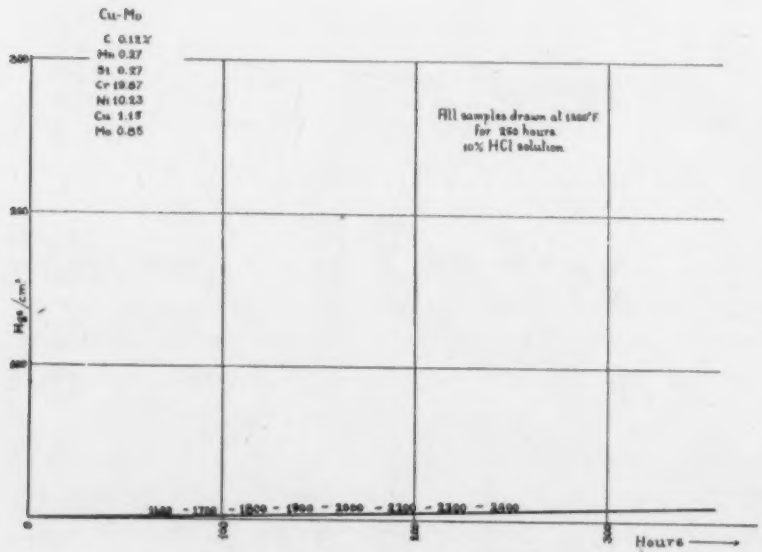


Fig. 23—Corrosion Rate of 18-8 Alloy Containing Additional Copper and Molybdenum, in 10 Per Cent Hydrochloric Acid Solution.

found that in plain 18-8 it occurred not at the hottest zone, but within the range between 1420 and 1350 degrees Fahr. In case of the alloy which contained approximately 1 per cent copper and 1 per cent molybdenum the break occurred at the hottest portion. Its strength (as measured by this test) is several times that of plain

18-8,[12] as is seen from Fig. 24. Microscopic examinations of numerous samples clearly show the presence of decomposition at grain boundaries of precisely the same appearance as in plain 18-8 (magnetic after decomposition) and in 18-8 with special additions (nonmagnetic after decomposition). It cannot be denied that the strength of the tested steels was affected to a different degree; yet,

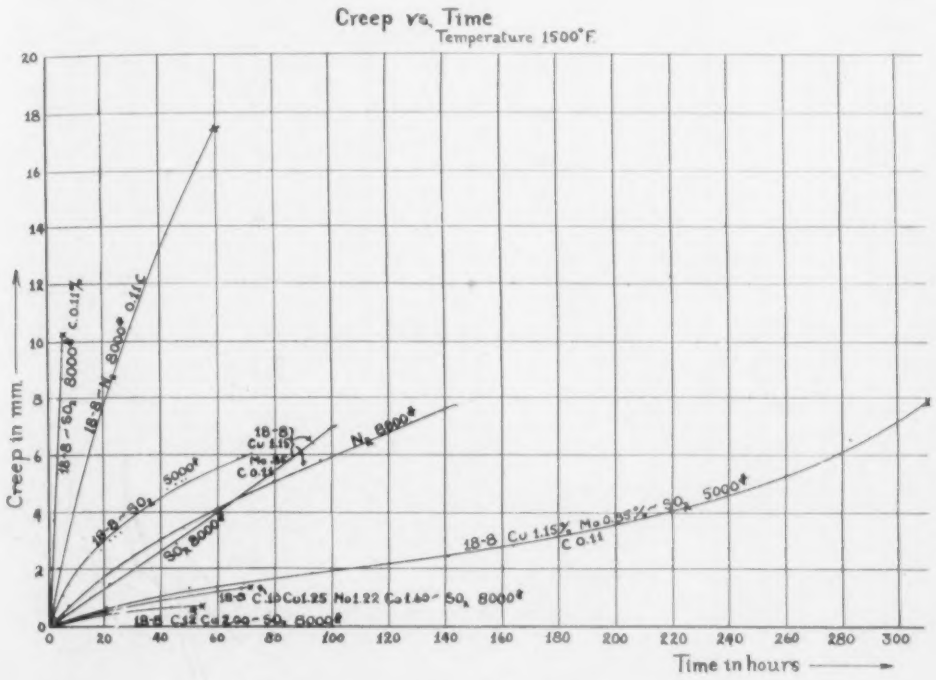


Fig. 24—Creep Versus Time of Nickel-Chromium Alloys.

let us again refresh our memory, the above mentioned steels showed up equally badly in the copper sulphate test. The length of the period of decomposition, as for example, in actual service, may be of much importance and must be considered.

Naturally, no attempt is being made to discredit the copper sulphate test. However, the observations here presented warrant a cautious attitude. After all, it is not in the interests of the consumer to disqualify, by artificial and drastic tests, the steels and alloys which might well serve the purpose; providing, of course, that the characteristics of such alloys and the conditions of service are carefully studied and sufficiently understood.

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[12]As this paper was being completed the results on 18-8 Mo, 18-8-Cu, and 18-8-W became available and indicated the same trend.

VIII. Influence of Preceding Treatments on Decomposition

During this investigation it was found that the treatment which 18-8 alloys received prior to the decomposition process, influences the latter to a marked degree. Due to the vast amount of data accumu-

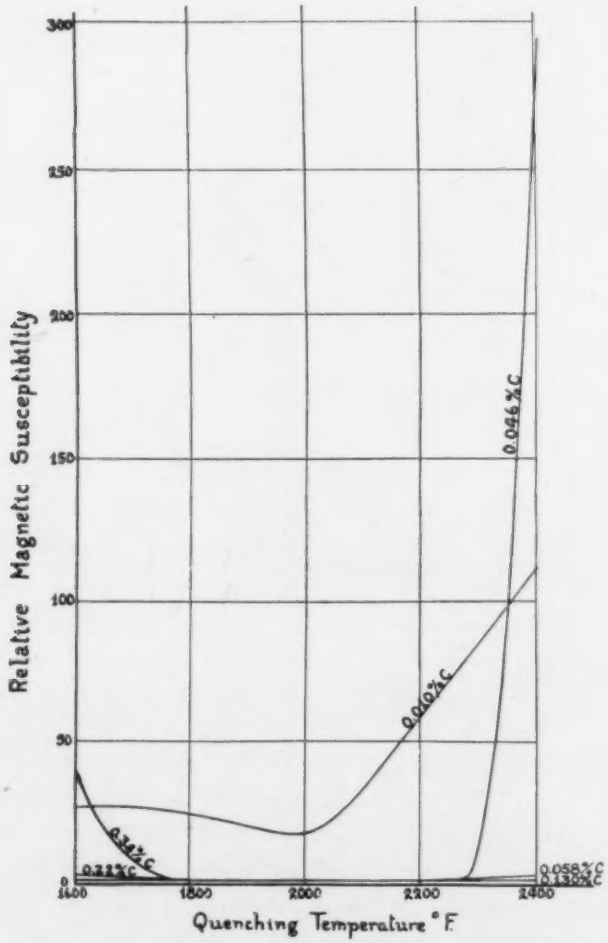


Fig. 25—Magnetic Characteristics Plotted Against Temperature for 18-8 Alloys.

lated it appears advisable to take it up in a form of conclusions, rather than a discourse.

It is admissible that 18-8 alloys as handled in commercial practice may contain some (and at times a considerable amount) of free carbides. The rate at which these carbides go in solution and, therefore, the homogeneity of the alloy (which, in turn, governs the phases present) depends on the quenching temperature. If magnetic characteristics of a given alloy are plotted against quenching

temperature several typical curves are obtained, each curve representing an alloy within a certain range of carbon composition. These curves, replotted from actual magnetic curves, are shown in Fig. 25. A typical curve for low carbon alloy (0.01 to 0.04 per cent) will show the magnetic phase present in all samples that were quenched at temperatures from 1600 to 2400 degrees Fahr. And, also, that

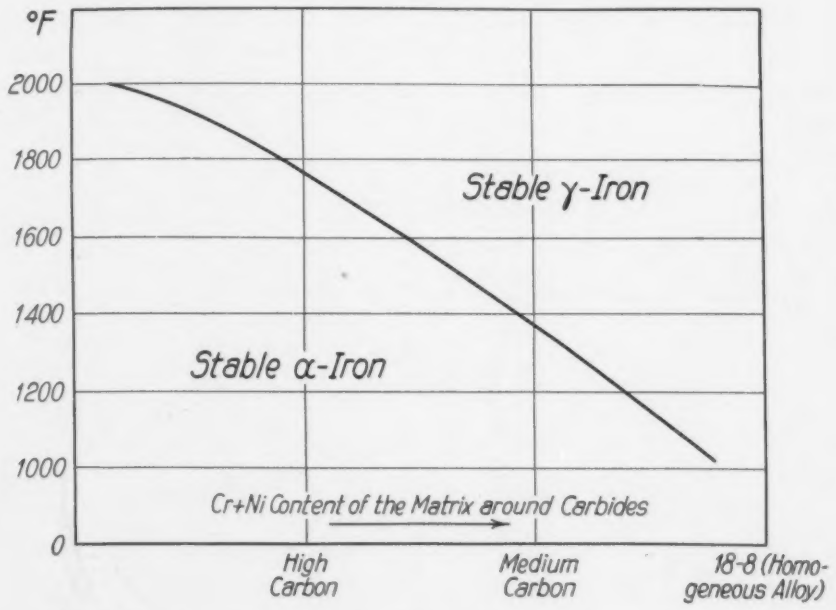


Fig. 26—Hypothetical Curve Showing the Areas Around Carbides Depleted in Chromium and Nickel Content.

the amount of this phase will increase with the increase in quenching temperature; for convenience we may call it "high temperature magnetic phase." Such an increase should be expected from the consideration of carbon-chromium-nickel-iron diagram.

The same phase is found, but to a much smaller degree, in alloys with 0.06 per cent carbon. As carbon is further increased to about 0.13 to 0.15 per cent the high temperature magnetic phase does not exist unless the heating was carried close to peritectic reaction. But with the carbon content still higher, up to 0.30 to 0.35 per cent, the magnetic phase is again present, this time at low quenching temperature. It is not, however, a high temperature equilibrium phase artificially retained. It is unquestionably due either to incomplete resolution of carbides that have separated out prior to quenching, or to the separation of carbides, providing the carbon content of the alloy is far in excess of the solubility figure at the given temperature.

It thus appears that the magnetic phase in high carbon alloys represents the areas around carbides depleted in chromium and possibly nickel. Similar depletion, of course, takes place in alloys with medium carbon content, but on quenching the areas remained non-

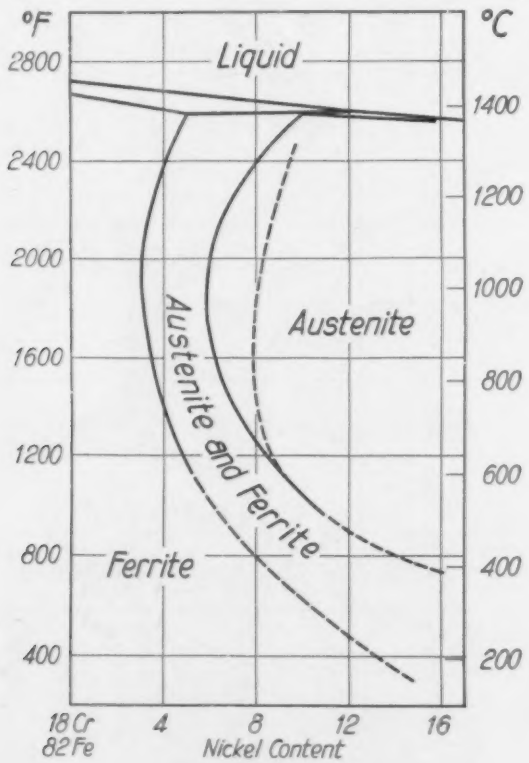


Fig. 27—Diagram Reproduced from Bain and Aborn and Corrected in Accordance with Present Findings.

magnetic, because of relatively smaller amount of depletion. A hypothetical curve in Fig. 26 serves to explain such a postulate.

Microscopic examination of numerous samples showed that the grain size is but little affected by quenching temperatures up to 2000 degrees Fahr. A marked grain growth occurs between 2000 and 2200 degrees Fahr. and continues up to 2400 degrees Fahr. The temperature of grain growth is independent of composition and remains practically the same for alloys with or without special additions. It was ascertained that free carbides (either in plain carbon 18-8 or in 18-8 with special additions) are all in solution between 2000 and 2100 degrees Fahr.

The question of grain size and of the resolution of free carbides

plays an important part in the process of decomposition. The samples in the "as quenched" condition were previously described as "non-attacked" by copper sulphate solution. The presence of the magnetic phase in some of these alloys is not contradictory to the behavior in the sulphate bath. We must not confuse local or "in spots" corrosion, which undoubtedly takes place in "as quenched" samples, with "intergranular" corrosion in samples after decomposition.

In the first part of this paper we had the occasion to state that the amount of carbon completely soluble in 18-8 austenite is quite low, even at elevated temperatures. As the quenching temperature is increased more carbon goes into solution and consequently, in the decomposition treatment we should have more carbides to come out. The expectation that the higher the quenching temperature, the more pronounced would be the decomposition, was fully upheld by microscopic examination. When the grain growth begins to be easily noticeable, it naturally changes the amount of decomposed material. This is seen fairly well from the studies of magnetic curves.

An observation, at first considered an experimental error, must not be overlooked. It appears that decomposition will occur to a lesser or greater degree depending on quenching temperatures. In most cases, and the chemical analysis of the steel in question apparently is quite immaterial, maximum decomposition[13] will occur when the steel is quenched from about 2000 degrees Fahr., sometimes a little lower or a little higher. This observation, as was just mentioned, was at first taken as an experimental mistake. Different measurements obtained at different times and by different manipulators could hardly be questioned. The observed maximum holds for low, medium, and fairly high plain 18-8, also for alloys with additions, such as cobalt, copper, molybdenum, etc. The magnitude is in most cases quite large but may be quite small. The maximum point is, as a rule, reached rather suddenly. It may be somewhat shifted depending on the temperature of decomposition (tempering). The complexity arising from various independent factors is such that it would be rather unwise to attempt to lay out general rules.

It is closely connected with such considerations as (a) original heterogeneity in the matrix, (b) solubility figures, (c) tendencies for precipitation of carbides, (d) the amount of carbides precipitated,

[13]In the sense of magnetic characteristics. Obviously, magnetic measurements are by far the most exact and reliable.

Table VII

Susceptibility to Decomposition Under Varying Conditions

	Initial Quench. Temp.	Decomp. Temp.	Re-quench. Temp.	Relative Magnetic Susceptibility After Decomp.	Relative Magnetic Susceptibility After Re-quench.	$CuSO_4$-H_2SO_4 Corrosion After Decomp.	$CuSO_4$-H_2SO_4 Corrosion After Re-quench.
0.13% Carbon	1600	1200	....	33.20	.....	A	..
	1600	1200	1300	29.90	29.80	A	HA
	1600	1200	1400	30.60	33.20	A	HA
	1600	1200	1500	33.20	6.28	A	N
	1600	1200	1600	45.60	2.73	A	N
	1600	1200	1700	44.00	1.72	A	N
	1600	1200	1800	32.00	1.06	A	N
	1600	1200	1900	24.50	1.37	A	N
	1600	1200	2000	31.00	1.44	A	N
	1600	1200	2100	32.70	1.43	A	N
0.22% Carbon	1600	1200	....	28.30	.....	HA	..
	1600	1200	1400	28.30	28.60	HA	A
	1600	1200	1600	36.30	9.90	HA	N
	1600	1200	1800	38.60	1.10	HA	N
	1600	1200	2000	34.80	0.66	HA	N

All samples held at quenching and re-quenching temperatures for half an hour. They were decomposed by holding at 1200 degrees Fahr. for 100 hours.

(e) the velocity of diffusion of different elements, etc. Obviously any theory would be of the nature of pure speculation. However, for a steel of a certain composition the conditions of treatment which would give the least amount of decomposition, could be ascertained experimentally[14]. The writer does not know whether this maximum (or minimum) is maintained when the period of decomposition is prolonged and is, therefore, unprepared to state whether this observation will be of practical importance.

It is important to know that harmful decomposition occurs very readily. Ordinary furnace cooling is sufficient to render 18-8 liable to attack by copper sulphate. The following table may be of interest.

Carbon 0.13 per cent, 18-8 alloy	Magnetic Characteristics	Corrosion
Heated to 1800, held 3¼ hrs.—water quench	0.76	N
Heated to 1800, cooled with the furnace to 1600°F water quench.	1.19	N
Heated to 1800, cooled with the furnace to 1400°F water quench.	29.60	SA
Heated to 1800, cooled with furnace to 1200°F water quench.	65.90	A
Heated to 1800, cooled with furnace to room temperature	66.50	A

[14]In certain cases low temperature either water or air cooling may be recommended because the mere presence of carbides undissolved in requenching is considered much less harmful than the greater precipitation, which, as was mentioned before, increases with increasing temperature (up to 2000 degrees Fahr.).

That by a simple heat treatment the noncorrosive characteristics of the alloys can be restored is quite well known. This experiment was performed in our laboratories and the results are worthy of thought. The details of experimentation are contained in the Table VII.

A sudden change in magnetic characteristics, accompanied by just as sudden change in sulphate corrosion properties, is indeed intriguing. Let us bear in mind that these changes are brought about by relatively small changes in temperature, approximately 100 degrees Fahr. If the whole process of decomposition is dependent upon carbide precipitation and is one of the necessary postulates, then on reversing the process, that is on reheating, we should not have expected to find such a narrow limit of temperatures within which the rate of diffusion is so abruptly changed. It appears again, as was maintained throughout the paper, that precipitation of carbides alone does not explain satisfactorily the intricate process of decomposition. In other words, that the phase change does not play a subordinate part, but is just as important, if not more so, than carbide precipitation.

It is not assumed that this paper, in which we tried to present in condensed form some information believed to be interesting, answers all of the pertinent questions regarding decomposition. The material collected and herewith presented appears to sketch the lines of defense against decomposition. The writer will be grateful to all those who would wish to cooperate with him in the work to follow.

Acknowledgments

It is with sincere appreciation that the author thinks of the friendly cooperation from Dr. M. A. Grossmann and Mr. Joublank of the Republic Steel Corp., Dr. Gregory Comstock, Firth-Sterling Steel Co., V. B. Browne, Allegheny Steel Co., Dr. Allison of the Crucible Steel Co. of America, and O. V. Greene of the Carpenter Steel Co. Through their cooperation various heats of steels were available for investigation. The most generous cooperation of Dr. Grossmann and Mr. Joublank must be especially mentioned. Dr. Paul Merica and Dr. F. M. Becket were most kind in supplying special electrolytic nickel and chromium.

It was through the extreme courtesy of Dr. F. Allison of the Crucible Steel Co. of America that magnetic measurements were

secured. The interest shown by Dr. Allison and his cooperation are most appreciated.

It is wished to express the appreciation of the cooperation from the Colonial Steel Company, Pittsburgh, which consisted in supplying material for the investigation, making most careful chemical analyses, and otherwise cooperating in every possible way.

Dr. F. M. Walters, Director, Bureau of Metallurgical Research, was very generous with his help in preparing two pure alloys and editing the manuscript. Mrs. Norman Hill Dawes, a colleague of the writer, is responsible for microscopic work, while R. S. B. Cook has taken care of the drawings.

Finally, the writer wishes to express sincere appreciation for the opportunities to discuss the work with Dr. M. A. Grossmann and Dr. John A. Mathews, his esteemed friends.

DISCUSSION

Written Discussion: By John A. Mathews, vice-president, Crucible Steel Company of America, New York City.

I have read this paper not only once but several times with very great interest, together with the papers by Newell, Luerssen and others submitted at this meeting, which go to show that the metallurgy of the corrosion-resisting alloys is "becoming no simpler fast."

The paper confirms my opinion that the question of intergranular corrosion cannot be dismissed simply by saying that the steel has become magnetic or that carbides have been precipitated, either with or without the assumption of chromium impoverishment in local areas. I cannot agree with Dr. Krivobok's criticism of the Strauss solution (copper sulphate plus sulphuric acid). It seems to me this is a particularly good test because it tells us exactly what we want to know, i.e., whether the steel is or is not subject to intergranular attack. The test is highly selective because it apparently attacks the grain boundaries or intergranular surfaces and not the main mass of the steel itself. It is quite likely that there are other electrolytes which will produce the same result but may require a long time to do so. It is also quite likely that steels which may prove subject to the Strauss solution would last indefinitely under certain other conditions. The use of 10 per cent hydrochloric acid does not appeal to me as a good substitute. The action of hydrochloric acid is not selective but more in the nature of a general solvent for both intergranular material and the grains themselves.

There are many chromium-nickel compositions of the more stable austenitic character than the customary 18-8 alloys which cannot be turned magnetic by heating to 1200 degrees Fahr. but which are, nevertheless, subject to intergranular attack. It is still evident that wherever it is commercially possible it is safest to subject the material to a high temperature anneal after it

has been subjected either locally or all over to temperatures in the 1000 to 1400 degrees Fahr. range. In the construction of large apparatus, particularly by the welding method, this frequently becomes impossible. In such conditions we must furnish materials not subject to intergranular corrosion even after they have been reheated within the breakdown zone temperature, but for the sake of determining whether such materials are or are not subject to intergranular attack the writer prefers to use the Strauss solution because of its specific effect and its searching character.

In addition to that I would like to add that we have alloys which have been welded and subjected to this test and we have nonmagnetic ones which are entirely free from any attack whatever. We have feebly magnetic ones which are entirely free from any attack and we have some strongly magnetic alloys which are equally resistant, that is if we may assume 720 hours of continuous boiling (except for intermediate times at which we change the electrolyte) is sufficient to test it. All those who have made the test know that for certain materials one hour is quite sufficient to show the breakdown at the grain boundaries. The steels that I have in mind were tested continuously for one month, boiling with 10 per cent copper sulphate, sulphuric acid, and they are as metallic as the day they went into the test.

Written Discussion: By H. D. Newell, chief metallurgist, Babcock & Wilcox Tube Co., Beaver Falls, Pa.

Dr. Krivobok's contributions on the subject of chromium and chromium-nickel-iron alloys are always welcome and provide much food for thought. The magnetic susceptibility tests on the alloys under study provide a useful means of determining the extent of decomposition as influenced by composition and thermal treatment. Such decomposition, i.e., the formation of a magnetic phase, may proceed from the alloy being too near the boundary of martensitic alloys by virtue of original composition or from alteration in composition induced by precipitation of carbides.

From a practical point of view, phase change resulting from composition is interesting but does not interfere with many commercial applications of such altered alloys. Physical properties are not changed to any great extent and corrosion resistance is not likely to suffer. On the other hand, carbide precipitation, whether or not accompanied by increase in magnetic susceptibility, may make the alloy liable to disintegration under corrosive conditions. This is particularly true if stress is present. Such precipitation may also alter the physical properties.

In the course of our own investigations, which have closely paralleled Dr. Krivobok's, we have run corrosion embrittlement tests on numerous austenitic steel alloys. Some of these were plain chromium-nickel compositions in which the ordinary 18-8 ratio was varied to a considerable extent. Other 18-8 compositions containing various additional elements such as silicon, copper, molybdenum, vanadium, tungsten and combinations of these elements, were examined. Disregarding phase change produced by alteration in composition, it was found that a tempering treatment followed by corrosion would induce disintegration in all alloys in the presence of sufficient carbide.

Many of the alloys with added elements and in the heat treated state were

much more corrosion resistant to the action of mineral acids than ordinary 18-8, but after tempering they showed no advantage from the standpoint of intergranular attack. There are two fields of application for stainless alloys in the class investigated by Dr. Krivobok. In one field there are mechanical and corrosion resistant applications at temperatures below a point where carbide precipitation can cause damage. In this field correctly heat treated alloys are applied and composition may be altered to provide suitable corrosion resistance for the intended service. The presence of a magnetic phase does not hinder application except in certain electrical uses and as it can be easily compensated for by change in composition, it is of no moment. (Reference is made to cold-worked low carbon 18-8 alloy which has increased in magnetic susceptibility due to formation of alpha iron.)

In the other field of use, where the alloy is in elevated temperature service, fine carbide precipitation can quickly render the alloy unsafe or cause rapid failure by disintegration providing conditions of stress and corrosion prevail. This is also true of welded structures which have not been heat treated prior to service.

Lowering of the carbon content of alloys applied in this second class of service has done more toward eliminating failure from disintegration than any additional elements added. We cannot agree with Dr. Krivobok's statement that mere lowering of carbon content does not render the alloy immune from destructive decomposition. In the past three years there has been manufactured several thousand tons of 18-8 alloy for elevated temperature service in which the carbon content has been limited to a maximum of 0.07 per cent. This effort on the part of the steel makers has done much toward ensuring satisfactory service for the alloy. This low carbon alloy has been used in many high temperature applications involving stress and corrosion and although it shows decomposition as measured by magnetic tests, it is quite satisfactory from both a physical and corrosion standpoint.

The writer has called attention[1] to the fact that grain size as well as carbon content influences the ability of the alloy to stand intergranular corrosion after heating in the carbide precipitation range. Fine-grained low carbon content alloys resist such corrosion better than coarse-grained alloys, by virtue of having a greater "grain boundary extent" to receive the precipitated carbides. It is wondered if Dr. Krivobok considered the effect of grain size in this light in his investigations.

Concerning the copper sulphate test, while it is admittedly drastic, 18-8 alloys which have been heated sufficiently to permit carbide precipitation are likely to fail under much milder corrosive agents. Many of the higher carbon alloys, 0.08 per cent and above, if tempered at 1200 degrees Fahr., will disintegrate in such agents as acetic acid, hot salt water and even tap water on long periods of exposure. Consideration of carbon content, grain boundary extent and resistance to copper sulphate after carbide precipitation are pertinent to the satisfactory service of 18-8 alloy for elevated temperature service. The correlation of gas corrosion tests at elevated temperature and the copper

[1]H. D. Newell, "Influence of Grain Size on the Properties and Corrosion Resistance of the 18-8 Iron-Chromium-Nickel Alloy for Elevated Temperature Service," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 673.

sulphate test after heating 18-8 alloys would do much toward enabling one to accurately select an alloy for a given service. In this respect, the influence of stress is of prime importance.

Dr. Krivobok's production and investigation of alloys containing about 0.01 per cent carbon are extremely interesting. The writer will look forward to the time when such alloys are available commercially, as then, with certain adjustments in alloy content, we will have a material not subject to decomposition regardless of thermal treatments.

In conclusion, I would like to congratulate the author and his co-workers for this interesting and useful contribution to the subject of iron-chromium-nickel alloys.

Written Discussion: By Albert Sauveur, Gordon McKay Professor of Metallurgy and Metallography, Harvard University, Cambridge, Mass.

When we are told that in the course of the investigation reported by the authors more than 500 samples were tested and studied, we are impressed by the amount of labor involved and this adds to our high appreciation of this important paper. Chromium-nickel steel of the type investigated by the authors has for some time occupied a conspicuous position on the metallurgical stage and we should be indebted to them for the additional light they have thrown upon its behavior. It is obvious that if its "decomposition" could be controlled or prevented, its commercial value would be materially increased. In order to do so, however, it is essential, as the authors clearly see, that we should know the cause of the phenomenon.

This 18-8 steel at a high temperature is a solid solution of carbon, nickel and chromium in gamma iron. This solid solution is stable above the transformation point of gamma iron. In pure iron the transformation occurs in the vicinity of 900 degrees Cent. (1650 degrees Fahr.). The presence of carbon, nickel and chromium, however, lowers the transformation point to some 650 degrees Cent. (1200 degrees Fahr.). Above that temperature, the alloy is stable and does not exhibit any tendency to decompose. On reaching 650 degrees Cent. (1200 degrees Fahr.) or thereabouts, the alloy becomes unstable and a long sojourn at that temperature results in decomposition. The mechanism of that decomposition is similar to the one observed in the breaking up of any solid solution on reaching its critical point. A new phase comes into existence—the alpha phase—around the grain boundaries and along some crystallographic planes. As the alpha phase, however, is not capable of retaining any appreciable amount of carbon in solution, carbides are precipitated. This is why the phenomenon has come to be known as carbide precipitation. In the absence of carbon or when only an extremely small amount is present, the decomposition proceeds in the same manner through the formation of the alpha phase, but necessarily there is little if any carbide precipitation. This alpha phase, necessarily free from carbides, is what the authors call "magnetic chromuim-nickel ferrite." That such decomposition of the solid solution does not occur at temperatures considerably below 650 degrees Cent. (1200 degrees Fahr.), although it is then more unstable, must be ascribed to lack of plasticity. The same phenomenon is observed in hardened steel. The retained austenite which is present is unstable, but lack

of plasticity does not permit its transformation. It does transform, however, at higher temperatures.

If this conception is correct, it follows that in order to prevent decomposition one or more elements should be added capable of producing a solid solution which will remain stable until a temperature is reached too low to permit decomposition.

Written Discussion: By Dr. B. Strauss and Dr. P. Schafmeister, Fried. Krupp A. G., Essen, Germany.

The accomplishments of Dr. Krivobok and his co-workers on "Further Studies on Chromium-Nickel-Iron and Related Alloys," continues the series of his work (together with Dr. Grossmann) on these alloys and furnishes very interesting further information. The question of intercrystalline corrosion on iron-chromium-nickel alloys is too complicated to be handled thoroughly in a short discussion. Permit us, therefore, to call attention to the complete work of Dr. Schafmeister and Dr. Houdremont on intercrystalline corrosion soon to appear in print.

Written Discussion: By F. H. Allison, Jr., Crucible Steel Co. of America, Pittsburgh.

The present paper by Dr. Krivobok and his associates holds a wide interest. It is especially interesting to the steel makers whose attention has been engaged for a considerable period of time in the subject of intercrystalline attack which occurs under certain conditions in the corrosion resisting chromium-nickel-iron alloys. While, as yet, the exact physical-chemical cause for the decreased corrosion resistance at the grain boundaries has not been determined, enough work has been done so that there is commercially available, 18-8 alloys which are completely invulnerable to this attack.

The comments on the use of the boiling copper sulphate test are noteworthy. The test has met considerable justifiable criticism on account of the drastic nature of its attack, the severity of which is seldom encountered in practical application. The merit of the test seems largely to be that steels which are found resistant to it are certain to withstand the milder forms of attack usually met with in service, although, for most applications, the test imposes an unnecessarily stringent requirement.

The authors' use of magnetic measurements in connection with the susceptibility to intercrystalline corrosion has been particularly interesting. It is evident that the relationship of the magnetic properties to the susceptibility to intercrystalline attack requires a large amount of further study. The small magnitude of the magnetism in the austenitic steels and the extreme sensitiveness of magnetic properties to a great number of conditions may easily cause any relationship which exists to be obscured. Cold work has an immense effect on the magnetic induction which is not limited to the grain boundaries. It is well known that cementite possesses magnetic properties. Thus the magnetic induction of the free carbides requires investigation before an increase in the magnetic properties of the alloys can always be attributed to an increase in alpha constituent. Grain size has been credited with playing a part in the susceptibility of the alloys to intercrystalline corrosion. It has not been demonstrated that this factor influences the magnetic results to an

observable degree. There is the further fact, which is brought out by the present paper, that composition greatly influences the magnetic properties without eliminating the susceptibility of the alloys to intercrystalline attack. The variation in magnetic induction which the authors find with constant reheating temperatures and varying quenching temperatures is an indication of the complexities which require solution. The relationship of the magnetic properties to the resistance to intercrystalline corrosion is further complicated by the difficulty of obtaining an exact index of the degree of intercrystalline corrosion. The methods of measurement of the attack at present are more of a qualitative than quantitative nature. The authors have not made clear the method used in measuring the depth of attack reported in the present paper.

The paper covers an exceptionally wide scope and has entailed a great amount of experimental work. Under such conditions it would have been impossible in the available time for the authors to follow all the interesting leads which presented themselves. There is one further consideration, however, in the problem of intercrystalline corrosion besides the possibility of chromium impoverishment and phase change which deserves attention. This is the effect of colloids in solid solution. Many valuable facts concerning colloids existing in a liquid medium have been reported, but few data are available regarding colloids in a solid matrix. The large amount of surface energy of the finely precipitated carbides should have considerable influence on the electrochemical properties of the solid solution. An investigation of the magnetic and corrosion resisting properties of the several alloys at smaller temperature intervals between 900 and 1500 degrees Fahr. might not only throw more light on the relationship between the magnetic induction and intercrystalline corrosion, but would also contribute some information regarding the effect of the size of the carbide particles. A study of the influence of time at heating at the carbide precipitating temperatures, which Dr. Krivobok promises, should also be particularly valuable in this respect.

Written Discussion: By Robert F. Mehl, assistant director, research laboratories, The American Rolling Mill Company, Middletown, Ohio.[2]

It is pleasant though difficult to accept Professor Krivobok's invitation, and to prepare a discussion of his paper,—difficult because of the encyclopedic thoroughness of his studies.

In all work where decompositions in solid phases are encountered, one fact is outstanding: the new phase or phases often appear preferentially at grain boundaries. Ordinarily the metallurgist ascribes this behavior to a higher degree of instability at the grain boundary, but this is hardly more than the introduction of new descriptive terms, and it devolves upon the scientist to discover and to formulate the basis for this instability. Ordinarily grain boundary distortion is postulated, and it is quite certain that the field of force in the surface of a grain (at the grain boundary) is quite different from that within the grain. If this unbalance in the force field at the boundary should lead to lattice distortion, as it surely must, it is reasonable to sup-

[2]Dr. Mehl is now director of the Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh.

pose that the solid solubilities at the boundary are different than within the grain, resulting in precipitation at the boundary and not within the grain, or at the boundary before within the grain; furthermore, this distortion must alter the rate of diffusion which controls the rate of precipitation. It might also be recalled that Willard Gibbs derived thermodynamic expressions for the concentration of a solute at the surface of a solution. Since the physico-chemical analogies between liquid and solid solutions are so complete, it is likely that a similar concentration of solute occurs at the surface of a grain, leading to an early precipitation at the boundary. It has not been demonstrated that such a concentration does in fact obtain, nor does there appear to be any way of predicting the extent of such concentration, yet this effect may be present in such decompositions as those described in Professor Krivobok's various papers.

The magnetic method used to follow the course of decomposition seems very suitable. I should like to enquire of Professor Krivobok whether he has thought of using X-ray diffraction methods in this study. Modern technique will permit the detection of small amounts of precipitate, and will also indicate the course of precipitation by changing lattice parameter and by lattice distortion. It is possible that this type of study would yield a more exact correlation with the corrosion of the alloys than was possible with a study of magnetic changes.

Written Discussion: By O. V. Greene, metallurgical department, the Carpenter Steel Company, Reading, Pa.

We are indebted to Dr. Krivobok for further information in regard to the peculiarities encountered with the 18-8 and related alloys when exposed to high temperatures. We have found that the copper sulphate test as described in the present paper requires long periods of time to differentiate between various treatments, unless the alloy in question is in such a condition that intergranular corrosion will take place in a matter of 40 to 50 hours. We feel that the Dupont nitric acid test as described by W. R. Huey[3] is not only considerably faster, but will determine quantitatively the differences that neither the acid copper sulphate nor the HCl tests will show. This test employs 65 per cent nitric acid by weight used boiling. Specimens are carefully polished and exposed to the action of this corrodant for five 48-hour periods. The corrosion rate is reported in inches penetration per month which can be calculated from a formula given in the paper referred to. We have made a considerable number of determinations by this method and find that the results are consistently accurate and can be checked.

In the accompanying table results of this test on a number of alloys in various conditions are given.

Irrespective of carbon content all of the alloys show the best corrosion resistance in the water-quenched condition. It is interesting to note that air-treating produces only approximately 1/10 of the corrosion resistance shown by water quenching from the same temperature. In our work with acid copper sulphate such differentiations could not be found.

On page 57 of the paper, the statement is made that the maximum de-

[3]W. R. Huey, "Corrosion Test for Research and Inspection of Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 1126.

No. Alloy	C	Si	Cr	Ni	Treatment	Corrosion Rate Inches Penetration Per Month
1	0.031	0.23	17.58	8.09	As rolled and reheated to 1100 degrees Fahr. Held 24 hours.	0.036900
1					As rolled and reheated to 1200 degrees Fahr. Held 24 hours.	0.011940
1					As rolled and reheated to 1300 degrees Fahr. Held 24 hours.	0.006154
2	0.050	0.21	17.58	8.98	As rolled	0.002861
2					Water quenched from 2000 degrees Fahr.	0.001868
2					Water quenched from 2000 degrees Fahr. and reheated to 1200 degrees Fahr. Held 24 hours.	0.033480
3	0.067	0.30	19.25	10.00	As rolled	0.002612
3					Water quenched from 2000 degrees Fahr.	0.001065
3					Water quenched from 2000 degrees Fahr., reheated to 1200 degrees Fahr. Held 24 hours.	0.064130
4	0.090	0.24	19.73	9.98	As rolled	0.022340
4					Water quenched from 2000 degrees Fahr.	0.001260
4					Water quenched from 2000 degrees Fahr., reheated to 1200 degrees Fahr., held 24 hours.	0.069510
5	0.105	0.44	17.95	9.35	Air treated from 2000 degrees Fahr.	0.017400
5					Water quenched from 2000 degrees Fahr.	0.000739
6	0.112	0.58	18.25	9.69	As rolled	0.038550
6					Quenched from 2000 degrees Fahr.	0.001465
6					Quenched from 2000 degrees Fahr. Reheated to 1200 degrees Fahr., held 24 hours.	0.092730
6					Water quenched from 1900 degrees Fahr., reheated to 1200 degrees Fahr., held 24 hours.	0.110200
6					Quenched at 2000 degrees Fahr. Reheated to 1200 degrees Fahr. Held 24 hours. Followed by reheating to 1600 degrees Fahr., held 24 hours.	0.007904
6					Quenched at 2000 degrees Fahr. Reheated to 1600 degrees Fahr. Held 24 hours.	0.008996
6					Brine quenched at 2000 degrees Fahr., reheated to 1200 degrees Fahr. Followed by 1600 degrees Fahr. Followed by 1200 degrees Fahr. (All temperatures used for 24 hour intervals.)	0.051395

composition will take place after quenching at 2000 degrees Fahr. followed by suitable reheating. From the data we have accumulated, quenching at 1900 degrees Fahr., with the same reheating temperature, seems to produce the same decrease in corrosion resistance as quenching at 2000 degrees Fahr.

The decrease in corrosion resistance after reheating at 1200 degrees Fahr. is apparent. In many cases after reheating in this temperature range, the alloys have only 1/50 of the corrosion resistance that they had in the quenched condition. The corrosion resistance as-rolled may lie between the air-treated and reheated specimens. However, occasional specimens as-rolled show a considerably better resistance than the air-treated ones. The influence of reheating at various temperatures and at different temperatures, one following the other, is also given. It is further interesting to note that decomposition takes place in all of these alloys irrespective of carbon content. The reheating temperature necessary to produce this condition apparently decreases with the carbon content.

Written Discussion: By M. A. Grossmann, metallurgist, Illinois Steel Co., South Chicago, Ill.

Dr. Krivobok is assuredly to be congratulated on the great amount of useful information furnished here. The paper brings out a number of points calling for additional comment.

The first point is on the relation between magnetic properties and corrosion. It is shown that the magnetic qualities of 18-8 may sometimes be taken as an index of probable corrodibility, while at other times they must not be so taken, and further that this relation between magnetic qualities and corrosion does exist when the carbon content of the 18-8 is high, and does not exist when the carbon content is low. This is an important point.

Again, it is very interesting to find the data on corrosion of alloys higher than 18-8. The data are in harmony with the conclusions on the effect of carbon, and dispose of the thought that mere increase in alloy content would eliminate corrosion.

Alsó, special attention must be called to the data on creep, which are summarized in Fig. 24, and which must have involved a tremendous amount of work. Because of the importance of the creep data, and because of the wide difference in behavior of the different alloys, it would be interesting to hear just how the creep was measured,—that is to say, the kind of instrument used.

In relation to the creep, it is interesting to hear that plain 18-8 broke, *not* at the highest temperature but in the intermediate temperature zone around 1400 degrees Fahr., which has been shown to be a temperature of decomposition, whereas the alloys which showed very little decomposition around 1400 degrees Fahr. broke in the normal manner,—that is,—in the hottest zone.

Oral Discussion

CHAIRMAN T. H. NELSON:[4] First, I would like to congratulate the authors on this splendid contribution. There is already voluminous literature

[4]Consulting metallurgist, Widener Building, Philadelphia.

on this subject. Secondly, in regard to some work that I have under observation at the moment which confirms the comments of Dr. Sauveur, and to some extent that of the author. I recently had the opportunity of examining 18-8 with carbon as low as 0.006 and 0.008. In that case we have a distinctly magnetic material. As you will note from some of my previous work, I had thought that magnetism was indicative of corrosive attack, but in this case we have strong evidence of magnetism without the intergranular corrosion in copper sulphate, and I am forming the opinion, which I think will check with Dr. Sauveur, that where we do have in the material both the gamma and alpha phase so long as the carbon is low at the same time, we do not get chromium impoverishment. Under these conditions it is possible for us to have a material magnetic embodying both alpha phase and gamma phase iron, but due to the low carbon content there is no chromium impoverishment; therefore we have a material containing two phases, both of which, however, have the requisite alloy content to render them corrosion resistant without any impoverished areas and so, despite the fact that the material may be so constituted and magnetic, we, nevertheless, are able to obtain satisfactory corrosion resistance from such a combination.

Authors' Closure

By V. N. Krivobok

Perhaps, after all, there is a slight misunderstanding between my esteemed friend Dr. Mathews and myself. I did not wish to propose substituting any other acid test, as for example hydrochloric acid, for the Strauss solution. In fact, I thoroughly agree with Dr. Mathews in regard to the apparent usefulness of this solution and its adaptability to many cases. I do maintain, however, that the Strauss test is an exceedingly severe one and must be specified (or adopted as a standard test) only when conditions of service warrant it. Unfortunately, its adoption as a routine test, regardless of the purpose for which the material is required, has become a serious question from the manufacturer's point of view. Since the presentation of the present paper on 18-8 quite a bit of work has been carried on in regard to the strength of various heat resisting alloys at high temperatures. Some of the modified 18-8 alloys compare exceedingly favorably with plain 18-8 (for that matter with plain chromium-nickel-iron alloys) showing high strength, even after prolonged heating within the dangerous zone 1200 to 1500 degrees Fahr. They are not immune to failure under the Strauss test, however, especially if heating, prior to the test, was of short duration. Their strength is such that the use of the material (for certain definite purposes) is obviously safe. The Strauss solution test precludes their use. Is it a good test, then?

There is little in the kind comments of Mr. Newell with which the present authors would not agree. Mr. Newell's work in the field of chromium-nickel alloys has equipped him with so much knowledge that his remarks are always interesting and pertinent. It is fully agreed that the phase change observable in some 18-8 with special additions does not interfere with many commercial applications of such alloys. It is not quite certain, however, that

"physical properties are not changed to any great extent" as Mr. Newell appears to believe. Recently a large amount of data was obtained pertaining to impact values of heat resisting alloys, some of which, upon reheating, suffer carbide precipitation while others merely undergo phase change. In both cases alloys have changed impact values very considerably. This information will constitute, it is hoped, a separate paper, and for that reason the details are not given here.

Again, as in my answer to Dr. Mathews, I have to take a position whereby I will appear as defending myself. Mr. Newell would not agree with the statement that mere lowering of carbon content does not render the alloy immune from destructive decomposition. Neither would I: for that very reason chromium-nickel alloys of exceptionally low carbon content (0.01 per cent) were prepared and studied. The fact that these alloys were found to be immune from carbide precipitation disease, proves that lowering of carbon content *below a certain amount* is a very helpful measure. Perhaps my fault lies in not stating more definitely (in the paper) that lowering of carbon content within *commercially possible* carbon limits does not render the alloy immune from destructive decomposition. Commercially made 18-8 cannot be guaranteed, to the best of my knowledge, with carbon less than 0.05 per cent. From the point of view of decomposition this is not low enough, but as I presented in the paper, laboratory metal with 0.01 per cent carbon is immune to decomposition.

In my work I did not consider the effect of grain size, but, having studied Mr. Newell's paper,[5] I fully agree with him that the grain size is apparently of much importance. It might please Mr. Newell to know—if he does not know it already—that in large industrial installations the grain size receives much attention.

After reading the discussion by Mr. Newell of the copper sulphate test, I take the liberty of surmising that he agrees with me, at least in that the sulphate test should be specified only when the conditions of service are of a nature that would warrant such a test.

I am indebted to Dr. Strauss and Dr. Schafmeister for calling my attention to the work of Dr. Schafmeister and Dr. Houdremont and its forthcoming publication. I shall look forward to seeing it.

I fully agree with the remarks by Dr. Allison, and thank him for the valuable suggestion. Indeed, the question of heat resisting alloys is very complex and for that reason alone, at least for me, it is so fascinating. The more I learn of the subject, the more I am inclined to agree with Dr. Allison that many conditions may and in fact do affect the magnetic properties of alloys and thus further complicate their studies. After all the question of magnetic properties is a question of equilibrium. And the latter, in turn, is a question of concentration, phase relationship and the rates of reaction. The time factor (the time at decomposition temperature) alone complicates the study of magnetic phase quite considerably,—as I already stated in my consideration of Mr. Newell's remarks.

The thought advanced by Dr. Allison in regard to the effect of colloids

[5]See footnote 1.

in solid solution is indeed worthy of consideration. I would indeed like to pursue this line of work but, frankly, I do not know the way of carrying it out.

It is a pleasure to hear from Dr. Mehl and I fully agree with his statement in regard to our insufficient knowledge concerning the exact state of the matter at the grain boundaries. The logic in the thoughts of Dr. Mehl cannot be disputed, but to have it proved or at least supplemented by experimental facts, is a difficult undertaking. While it is true, as Dr. Mehl stresses, that the physico-chemical analogies between liquid and solid solutions are so complete, yet it is apparently true that the experiments would have to be conducted by several generations consecutively, for the life of one man would not be long enough. What about the excellent work of Bain on rates of reactions in the solids? In the course of studies on the iron-manganese-carbon system the participating workers were faced with what appeared to be unsurmountable difficulties, as regards the state of equilibrium.

I have thought indeed of using X-ray diffraction methods in the study as recorded in the paper. I sincerely believe that the method would yield very reliable and indeed interesting results. Purely practical considerations, as is often the case, stood in the way of the realization of such studies. I must state, apologetically of course, that with some 500 samples, the X-ray diffraction method seemed to be out of the question.

The remarks of Mr. Greene are of much interest to me and I am indeed obliged to him for calling my attention to Mr. Huey's paper. Since reading the paper of Mr. Huey, I have conducted several tests using 65 per cent nitric acid by weight, and find that the results as given by Mr. Greene are quite reproducible. I was particularly interested in alloy number 1 given by Mr. Greene in his table. The carbon content of this alloy is stated to be 0.03 per cent,—very low indeed, and yet the alloy shows carbide precipitation and subsequent corrosion. Are we to interpret from these results that carbon as low as 0.03 per cent is still too high to permit the indiscriminate use of this material? Since the carbide precipitation apparently occurs in this alloy, it can mean but one thing, namely, that the solubility for carbon at 1200 degrees Fahr. is lower than 0.03 per cent. These results are also important in view of the statement recently made that the effect of carbon less than 0.04 per cent upon ordinary corrosion behavior is too slight to be observable.[6]

I have read with much interest the comments of my esteemed friend, Dr. M. A. Grossmann. The work which has been carried on since the preparation of the present article indicates that the relationship between corrodibility and magnetic properties is to be considered in terms of time. That is to say, at some stages of decomposition the relationship is fairly evident: but as the time increases and the homogenizing effects take place, this relationship is considerably altered. At least, it is unquestionably so in this case of special 18-8 (that is, those to which other elements were added).

In reference to the remarks made by Dr. Grossmann, concerning the creep (briefly summarized in Fig. 24 of the paper) it is hoped that the data now available will soon be presented in a separate publication. However, in

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[6]Aborn and Bain; "Nature of the Nickel-Chromium Rustless Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 18, July-December, 1930, p. 871.

answer to Dr. Grossmann's request, I wish to state that no attempt was made to measure the creep value in the strict sense of this word. The samples of special 18-8 were loaded with a certain static load (varying from 5 to 8000 pounds per square inch) and the automatic recording curves representing elongation versus time (until the samples broke) were obtained. The behavior of steel of various compositions is so different that I feel fully justified in performing this simplified test.

I am pleased to have the comments of my esteemed teacher, Professor Sauveur. His clear conception of the carbide precipitation phenomenon will be, I am certain, very helpful to all those who are engaged in the studies of heat resisting alloys. Perhaps I may permit myself this additional thought; I believe that not only the critical (transformation) point in chromium-nickel-iron alloy should be considered but also the solubility, at various temperatures, of carbon in solid alloy. The carbide precipitation can be produced by heating at any temperature between 900 and 1700 degrees Fahr. I feel reasonably certain that the same precipitation would occur even at lower temperature—the factor of time being all important—and so, the question of critical point becomes rather uncertain. The concept that two phases co-exist together—one stable and the other metastable—may be entertained. This concept, of course, does not contradict the one so clearly stated by Dr. Sauveur.

Of course I was interested to know from T. H. Nelson that his experiments with very low carbon 18-8 alloy fully substantiate our findings. In our case we did not observe much of the magnetic phase (chromium-nickel ferrite) except after the decomposition treatment which consisted of heating between temperatures of 1400 to 1600 degrees Fahr. It is very interesting to me that carbon as low as 0.006 per cent could be obtained. I would appreciate very much if Mr. Nelson would care to let me know how it was done and more particularly whether it was an experimental or commercial alloy. I wish to thank most sincerely all of the gentlemen for their friendly and interesting discussions.

SCALING OF STEEL AT HEAT TREATING TEMPERATURES

By Clair Upthegrove and D. W. Murphy

Abstract

This paper presents the results of an investigation of the relative scaling effects of atmospheres of air, carbon monoxide, carbon dioxide, and water vapor on steel over the temperature range 1000 to 2000 degrees Fahr. In addition the relative scaling effects of different gas-air ratios on steel at temperatures of 1500, 1600, 1700 and 1900 degrees Fahr. are given.

It is shown that scaling does not increase regularly with increase in temperature in the simple atmosphere, air, oxygen and carbon dioxide. A maximum and a minimum point are observed for carbon dioxide at 1400 and 1520 degrees Fahr. and for air at 1800 and 2000 degrees Fahr. A very definite retardation in the rate of scaling in oxygen is also observed at 1800 degrees Fahr., the temperature at which blistering first becomes noticeable in both air and oxygen. For temperatures below 1700 degrees Fahr. but very little scale is produced by combustion atmospheres carrying four or more per cent of carbon monoxide.

MUCH of the steel produced annually requires a heat treatment to produce the desired qualities in the finished product. With the exception of a few steels most heat treatments are accomplished in the temperature range of 1000 to 2000 degrees Fahr. (540 to 1095 degrees Cent.). Consequently the problem of the action of various atmospheres on steel arises. The principal effects of atmospheres on steel at these temperatures are those of decarburization and scaling. An extensive investigation of decarburization by W. E. Jominy[1] indicated that this phenomenon was in part dependent on the type of scale formed on the steel.

[1]W. E. Jominy, "Decarburization of Steel at Heat Treating Temperatures," University of Michigan, Engineering Research Bulletin No. 18.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, who are members of the society, Clair Upthegrove is professor, department of chemical engineering, and Dr. D. W. Murphy is research associate, department of engineering research, University of Michigan, Ann Arbor, Michigan. Manuscript received June 17, 1932.

Scaling, in addition to its effect on decarburization, has a direct bearing upon many of the items entering into the cost of heat treatment. There is, of course, the intrinsic value of the metal converted to scale which is, however, rather small in comparison with other effects directly attributable to scaling. The fact that oxidation occurs, requires the designer of a part to specify a certain tolerance in the dimensions prior to heat treating to compensate for the effect of scaling. Final machining of heat treated parts is thus made necessary to remove the excess metal which adds directly to the cost of the product. Furthermore, adhering bits of scale are the frequent cause of soft spots or poor hardening penetration. These are perhaps only a few of the ways in which scaling affects the cost of heat treatment, but they are sufficient to illustrate the importance of this problem.

Considering the importance of scaling there was relatively little information concerning the various factors which influence scaling at heat treating temperatures which could be applied in a practical way to minimize the detrimental effects. Therefore, for the past two years, the Committee on Industrial Gas Research of the American Gas Association has sponsored a program of research to bring to light more of the facts surrounding the problem of scaling. In this paper the results of a portion of the research are presented. In particular, following a brief discussion of the available literature and the methods employed in the present investigation, the data are presented which were obtained in studying the various factors influencing oxidation in simple gases together with a brief account of experiments in gas-air combustion atmospheres.

Literature

Previous research on the general subject of the oxidation of iron has proceeded along three rather distinct lines of investigation. The earliest researches aimed to determine the equilibria in the systems Fe:O:C and Fe:O:H. A number of empirical studies were later carried on in which the extent of oxidation was determined under very special conditions. The third class of researches comprises those in which the mechanism of oxidation was studied. For the present, discussion of equilibria will be omitted.

Among the empirical researches there are a considerable num-

ber of papers. Friend[2, 3] reported that oxidation of iron with steam began to be appreciable at 750 degrees Fahr. (400 degrees Cent.) and somewhat later that the influence of temperature and time were quite marked. His experiments led him to believe that the dissociation of water vapor played an extremely important part in the oxidation of iron by steam. Utida and Saito[4] observed the rates of oxidation of various materials in air by means of a thermo-balance measuring gain in weight. They found that the rate of oxidation decreases with increasing time. Scott[5] also studied the oxidation of iron and carbon tool steels in air, observing that Armco iron scaled faster than high carbon tool steels at the same temperature.

Marson, Angus and Cobb[6, 7] investigated the scaling of steel in steam, carbon dioxide and air at 1650 and 1830 degrees Fahr. (900-1000 degrees Cent.), observing that scaling was much increased at the higher temperatures. They rated air as the most powerful oxidizer, steam next and carbon dioxide, the least. Cobb and his associates also studied scaling in mixtures of carbon monoxide and carbon dioxide and of water vapor and hydrogen. Hatfield[8] also reported scaling observations in synthetic mixtures and in air. He observed that water vapor and sulphur dioxide were powerful in their effect on the oxidation of steel.

Dickenson[9] made a few tests of scaling in actual gas-air combustion atmospheres. His measurements lacked quantitative accuracy as did those of McCormick[10] who likewise investigated briefly the action of furnace gases on steel in the heat treating temperature

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[2, 3]J. A. N. Friend, Journal, West Scotland Iron and Steel Institute, Vol. 17, 1910, p. 66-69. *Proceedings,* Chemical Society, Vol. 27, 1911, p. 124, and *Journal,* Chemical Society, Vol. 99, 1911, p. 969-73.

[4]Yuhatiro Utida and Makoto Saito, "The Oxidation of Metals and Alloys at High Temperatures," Science Reports of Tohoku Imperial University, Vol. 13, p. 391-99.

[5]Howard Scott, *Chemical and Metallurgical Engineering,* Vol. 25, p. 72-74.

[6, 7]Marson, Angus and Cobb, *Journal,* Society of Chemical Industries, Vol. 46, p. 61T-72T, and *Forging, Stamping and Heat Treating,* Vol. 13, p. 118-123.

[8]W. H. Hatfield, "Application of Science to the Steel Industry," TRANSACTIONS, American Society for Steel Treating, Vol. 15, 1929, p. 474, 652, 817, 986.

[9]J. H. S. Dickenson, *Journal,* Iron and Steel Institute, Vol. 106, p. 103-41, and *Engineering,* Vol. 114, p. 326-378.

[10]G. C. McCormick, "Furnace Atmospheres and Their Relation to the Formation of Scale," TRANSACTIONS, American Society for Steel Treating, Vol. 2, 1921-22, p. 1006.

range. The empirical researches present no connected survey of the various factors influencing scaling and frequently the methods employed have not been of the highest possible accuracy.

Passing over many of the papers discussing the mechanism of oxidation, three may be cited as of the greatest importance. Pilling and Bedworth[11] after a careful investigation of the oxidation of copper advanced the hypothesis that continued oxidation of a metallic surface occurred by reason of the diffusion of oxygen inward through the previously formed layers of scale. They divided all metals into two groups, noble and base, depending upon the dissociation pressure of the oxides which tend to form. The base metals are further classified into two groups based upon the texture of the oxide coating and depending upon a certain relation between the densities of metal and oxide. The oxide texture determines in their opinion, whether or not the oxide coating will serve to decrease further oxidation. The controlling factor in oxidation is, according to this theory, the solution and the diffusion of oxygen through the layers of scale to the metal-scale interface.

Fedotjev and Petrenka[12] advanced the theory that the alternate formation and reduction of higher and lower oxides of iron was responsible for continued oxidation. In their mechanism they considered that FeO was formed first and then oxidized to Fe_3O_4. The Fe_3O_4 was then reduced by the iron in contact with it to FeO so that additional iron was oxidized in this process. The FeO was oxidized again to Fe_3O_4 and the process repeated.

Pfeil [13] however has advanced what appears to the authors to be the best mechanism. In his theory there is of course a diffusion of oxygen inward through the scale but in addition there is a diffusion of iron outward through the scale. In this manner it is possible to explain, without assuming extraordinary properties for the oxide, the growth of scale about foreign objects placed on the surface of steel prior to scaling without disturbing their original position.

While the mechanism by which continued oxidation occurs seems to be sufficient to account for the facts as known at present there is

[11] N. B. Pilling and R. E. Bedworth, *Journal*, Institute of Metals, p. 529-83.

[12] P. P. Fedotjev and F. N. Petrenka, *Journal*, Russian Physical and Chemical Society, Vol. 58, p. 222-8. *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 157, p. 165-72.

[13] L. B. Pfeil, "The Oxidation of Iron and Steel at High Temperatures," *Journal*, Iron and Steel Institute, Vol. 119, Part I, 1929, p. 501.

relatively little information available concerning the various factors bearing upon scaling. Past investigations have suffered by being carried out under very restricted conditions, with the result that such isolated observations are very difficult to correlate in a useful manner.

Method

The methods followed in this investigation, which have aimed at a thorough study of the factors influencing scaling in the temperature range 1000 to 2000 degrees Fahr. (540-1095 degrees Cent.), are in general quite similar to those used by Jominy and Murphy[14] and by Murphy, Wood and Jominy[15] in their studies of scaling at forging temperatures. The samples were heated in an electric tube

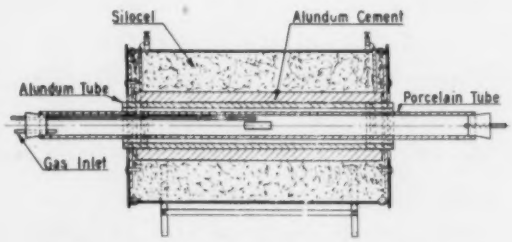


Fig. 1—Diagram of Electric Tube Furnace Used in this Investigation.

furnace which contained a long, glazed porcelain tube, approximately 2 inches in inside diameter. The furnace is shown in Fig. 1.

It was found necessary in order to facilitate the control of the temperature of the furnace to bring the weighed sample to heat in a stream of purified nitrogen. When the temperature of the sample had apparently attained equilibrium with the furnace temperature, the nitrogen flow was stopped and the chosen atmosphere was introduced through the tube provided for that purpose at the rear of the furnace. Timing of runs was started the instant the nitrogen was turned off, and stopped after the proper period of exposure, when the nitrogen was again turned on and the flow of the chosen atmosphere stopped. The sample was then immediately quenched in distilled water, stripped in an electrolytic cell and weighed. The loss

[14]W. E. Jominy and D. W. Murphy, "Scaling of Steel at Forging Temperatures," Transactions, American Society for Steel Treating, Vol. 18, 1931, p. 19.

[15]D. W. Murphy, W. P. Wood and W. E. Jominy, "Scaling of Steel at Elevated Temperatures by Reaction with Gases and the Properties of the Resulting Oxides," Transactions, American Society for Steel Treating, Vol. 19, 1931-32, p. 193.

in weight was expressed in terms of pounds per 100 square inches.

The scale split off during quenching was filtered, dried and weighed, as was that split off in the electrolytic pickling. The pickling bath, a 10 per cent solution of sulphuric acid in distilled water, was analyzed for iron, since some of the scale is dissolved in stripping. To maintain a check on the possible solution of the sample itself during stripping, a blank consisting of a previously stripped sample was suspended in the bath at the same time with the scaled sample. The final loss in weight could then be corrected by the amount of the change in weight of the blank. From the scale split off during quenching and stripping and the iron content of the bath the total weight of scale formed was obtained, and knowing this quantity it was possible to determine the percentage of the total scale split off during quenching which might be taken as an indication of the adherence of the scale. The scale was also analyzed for free iron, ferrous iron and ferric iron by treating one sample of scale with neutral ferric chloride to dissolve free iron and by titrating another sample of the same scale in sulphuric acid solution first for ferrous iron and then for total iron.

The samples were 2½ inches long and ⅝ inch in diameter, after machining and polishing with number 00 emery cloth. These were mounted on chromel A wire boats before placing in the furnace in order to keep the samples from touching the refractory tube. The analysis of the steel used in this research is as follows: C, 0.18 to 0.20 per cent; Mn, 0.45 to 0.48 per cent; Si, 0.17 to 0.22 per cent; S, 0.03 per cent or less; P, 0.021 per cent or less.

Results

The study of the various factors influencing scaling was accomplished under atmospheres consisting of pure gases alone or in combination with nitrogen. In this way the effects of velocity, temperature, time and partial pressure of the oxidizing gas have been considered. The second portion of the investigation deals with oxidation under more complex atmospheres which consist of mixtures of carbon dioxide and steam or of gas-air combustion atmospheres, using various ratios of air to gas.

Scaling in Simple Gases

In this portion of the work, the atmospheres used were dry air,

carbon dioxide, steam, oxygen and mixtures of the latter three with nitrogen.

Effect of Variation of Velocity of Flow of Gas. The data obtained in the experiments in which the velocity of gas flow was varied are summarized in Fig. 2. In the case of air and carbon dioxide increasing the velocity of the gas stream from 0 feet per minute to about 1 foot per minute increases the scaling losses very

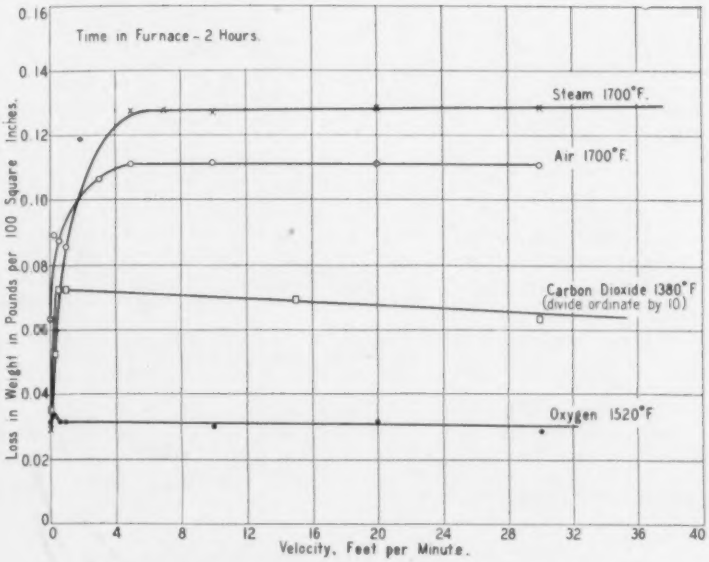


Fig. 2—Effect of Variation of Velocity of Gas Flow on Scaling of S. A. E. 1015 Steel.

markedly. In fact the carbon dioxide curve attains its maximum value with rates of flow of about ½ foot per minute and gradually decreases with increasing velocity. This decrease may possibly be due to the fact that the gas stream does not attain the furnace temperatures and consequently effects a slight lowering of the surface temperature of the sample. The air curve does not attain its greatest value until a flow of 5 feet per minute is reached.

The oxygen curve is interesting however because of the fact that there is no appreciable difference in scaling loss, between static conditions and a rate of flow of 10 feet per minute. The occurrence of the hump in this curve at very low rates of flow may be attributed to the heat developed by the reaction which would tend to increase the surface temperature. Hence with somewhat greater rates of flow this heat may be dissipated to the gas stream, thus causing a drop in the scaling loss.

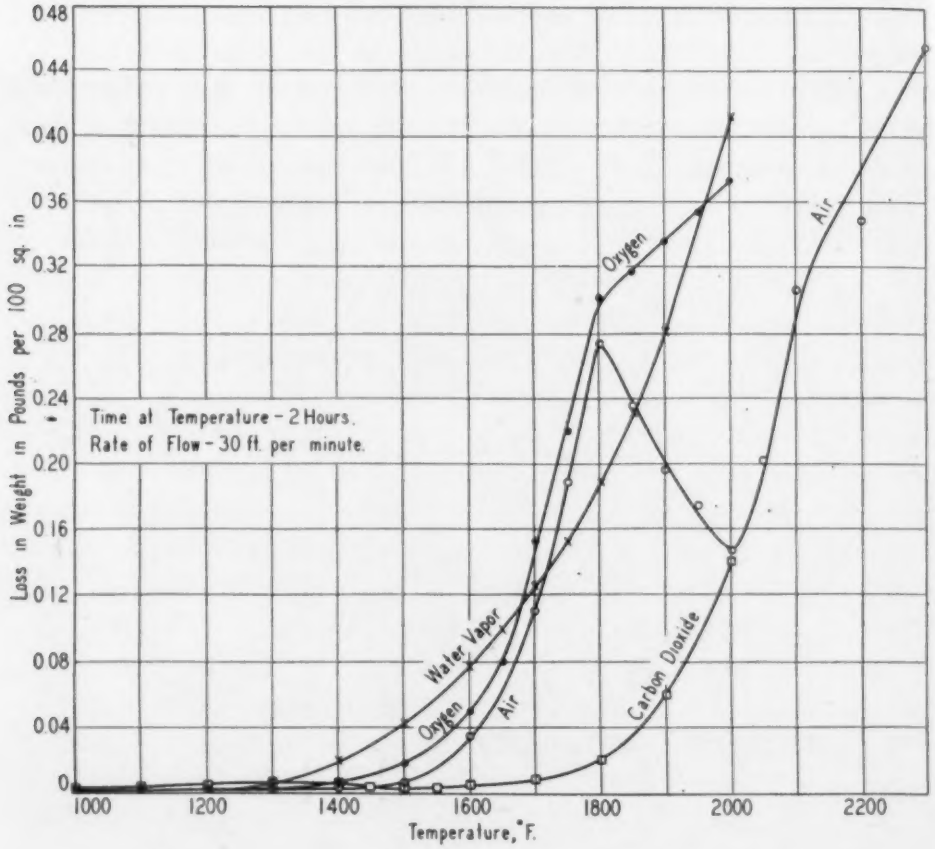


Fig. 3—Effect of Variation of Temperature on Scaling of S. A. E. 1015 Steel.

The steam curve is quite similar to the other three. It has been pointed out by Murphy, Wood and Jominy[16] that the type of curve shown in this figure is a result of the diffusional nature of the process of scaling. With very low rates of flow, except in the case of oxygen, the supply of the gaseous reagent is not sufficient to maintain the oxidizing reaction at its maximum rate for the particular temperature and hence increasing the velocity which increases the supply of reagent will tend to increase the amount of metal involved in scaling. However when the rate of supply becomes sufficient for the full requirements of the oxidizing reaction no further increase in supply could be expected to alter the amount of steel converted to scale.

Effect of Variation of Temperature. In Fig. 3 the data are summarized which were obtained when the temperature of exposure was varied from 1000 to 2000 degrees Fahr. (540-1095 degrees

[16]Loc. cit.

Cent.). Perhaps the most striking curves are those for air and oxygen which show marked changes at 1800 degrees Fahr. (985 degrees Cent.). In the case of air, scaling actually decreases with increasing temperature from 1800 to 2000 degrees Fahr. (1095 degrees Cent.), while on both sides of this region scaling increases with increasing temperature. In the case of oxygen the rate of in-

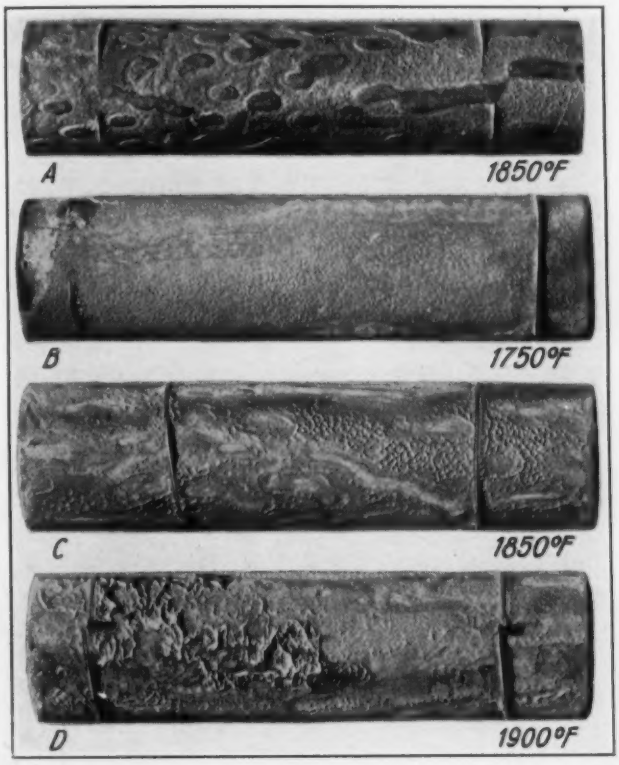


Fig. 4—Blister Formation on S. A. E. 1015 Steel in Oxygen Atmosphere. A—Sample Blistered in Oxygen at 1850 Degrees Fahr., After Removal of Scale. B, C, D—Samples Blistered in Oxygen, Scale Not Removed.

crease of scaling with increasing temperature does not become negative as with air but shows only a retardation of this rate with temperatures above 1800 degrees Fahr. (985 degrees Cent.).

This break in the oxygen and air curves coincides with the appearance of blistering of the samples. The blisters shown in Fig. 4 are areas which have not been subjected in the same degree to scaling reactions as have the neighboring areas. This results in leaving raised portions of metal in a type of bas-relief. According to Pfeil's theory, which has been supported by Murphy, Wood and Jominy, scaling occurs by the diffusion of oxidizing agent inward and by

the diffusion of iron outward. If either of these diffusional processes were temporarily hindered in certain areas the rate of scaling would be decreased at those places. Quite possibly the blister forms at a point and gradually spreads as the oxidation of the primary FeO first formed by the reaction proceeds rapidly to Fe_3O_4. Since the specific volume of Fe_3O_4 is greater than that of FeO it might be reasonable to expect that the scale in the regions rich in Fe_3O_4 would have some tendency to buckle away from the sample. The diffusion of iron outward in these areas would be interrupted, thus diminishing the scaling rate at these points and creating blisters. The scale at these blisters should then be higher in oxygen than the surrounding areas which has been confirmed in some instances where comparative analysis was possible. Pfeil has established the fact that scale and iron can react to form a scale of lower oxygen content even when not actually in contact. The reaction is much slower than the normal reaction but in time it will renew the contact between the raised portion of scale and the metal, reëstablishing channels for the diffusion of iron and consequently the normal reaction rate. However in that period of time scaling has progressed normally in the surrounding areas which would then create the bas-relief pattern of the blisters.

Other points of interest in the curves are the presence of a maximum in the carbon dioxide curve between 1300 and 1400 degrees Fahr. (705-760 degrees Cent.) and a corresponding minimum somewhat above 1500 degrees Fahr. (815 degrees Cent.). Following this region of irregularity the scaling losses increase quite rapidly with increasing temperature, especially from 1800 to 2000 degrees Fahr. (985-1095 degrees Cent.). Water vapor produces the greatest scaling losses in the region 1300 to 1680 degrees Fahr. (705-915 degrees Cent.), but at this point it is exceeded by oxygen. Water vapor again becomes more active than oxygen above about 1950 degrees Fahr. (1065 degrees Cent.). The only region in which air is noticeably more active than water vapor is that between 1720 and 1850 degrees Fahr. (935-1010 degrees Cent.). It might also be pointed out that between 1000 and 1300 degrees Fahr. (540-705 degrees Cent.) there is little difference in the scaling losses resulting in the various gases and that the scaling in any event in the four gases is nearly inappreciable.

In Fig. 5 is shown the effect of temperature on the average scale composition with respect to ferrous iron content. It will be seen that

the carbon dioxide curve has a pronounced maximum between 1300 and 1400 degrees Fahr. (705-760 degrees Cent.), and a pronounced minimum at about 1500 degrees Fahr. (815 degrees Cent.), after which the ferrous iron increases regularly with increasing temperature. It will be noted that the maximum and minimum of ferrous iron content coincide with the maximum and minimum of scaling loss in

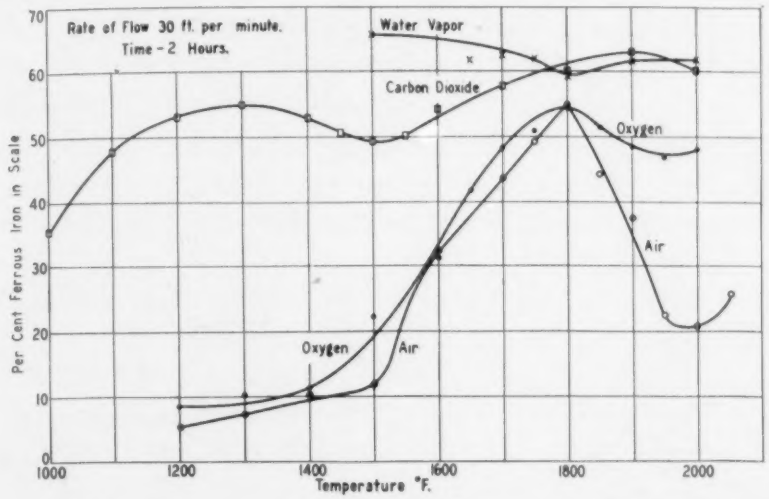


Fig. 5—Effect of Variation of Temperature on Composition of Scale.

carbon dioxide. The water vapor curve shows a slight irregularity in the neighborhood of 1800 degrees Fahr. (985 degrees Cent.), which is not evident in the scaling loss curve.

The oxygen and air curves again present interesting features when viewed from the standpoint of ferrous iron content. In the temperature region 1200 to 1800 degrees Fahr. (650-985 degrees degrees Cent.) the ferrous iron in both cases increases with increasing temperature. Where blistering begins to be appreciable, at 1800 degrees Fahr. (985 degrees Cent.), however, the tendencies are reversed and ferrous iron decreases with increasing temperature up to approximately 2000 degrees Fahr. (1095 degrees Cent.), the decrease in the case of air being much more marked than in the case of oxygen as was observed in the scaling loss curves. The decrease in ferrous iron content indicates that in this region a considerable portion of the scale is in a higher state of oxidation than FeO. It will be remembered that the explanation advanced for blistering involved the assumption that the areas of scale over blisters have higher oxygen contents than those surrounding the blisters. Consequently

an average sample of the scale from a blistered specimen should show a higher oxygen content coincidental with a lower ferrous iron content than a sample of scale from a specimen free from blisters. The curves are excellent confirmation of the hypothesis.

Effect of Variation of Time

The effect of variation of time on the scaling losses of S.A.E. 1015 steel is shown in Fig. 6. In the case of water vapor, air and oxygen the rate of scaling decreases with increasing time. The de-

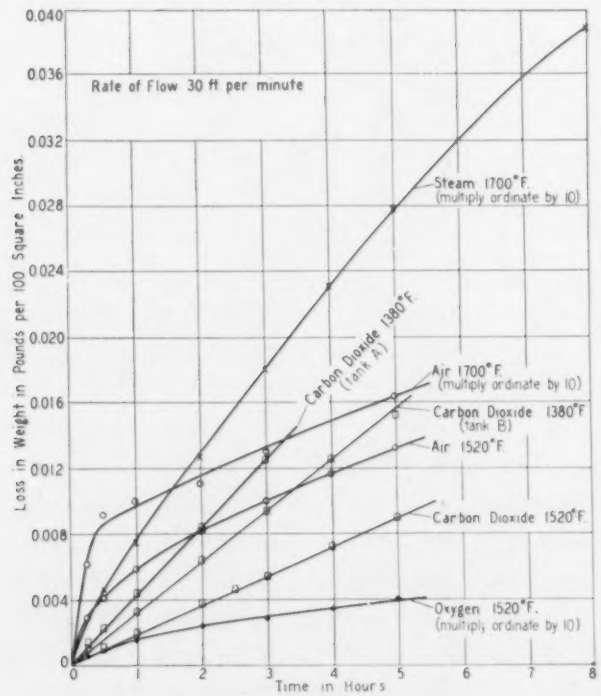


Fig. 6—Effect of Variation of Time on the Scaling Loss of S. A. E. 1015 Steel.

crease in the case of steam is very slight and at 1700 degrees Fahr. (925 degrees Cent.) the scaling in air is greater than that in steam for periods up to slightly over 2 hours while with times greater than 2 hours the scaling losses in steam greatly exceed those in air.

A comparison of the time curves for air at 1520 and 1700 degrees Fahr. (825-925 degrees Cent.) shows that time becomes an increasingly important factor at higher temperatures. Likewise a somewhat similar situation exists in the case of carbon dioxide. Here however curves for 1380 degrees Fahr. (750 degrees Cent.)

lie above that for 1520 degrees Fahr. (825 degrees Cent.) because of the presence of the maximum and minimum points in the temperature curve, Fig. 3. Above 1520 degrees Fahr. (825 degrees Cent.) it would be expected that increasing the temperature would also increase the importance of the time factor. At 1380 degrees Fahr. (750 degrees Cent.) two different tanks of carbon dioxide were used, differing chiefly in oxygen content. The curve resulting from Tank A having the greater oxygen content lies considerably above that for Tank B which shows the considerable effect of small amounts of impurities in gases on the scaling losses.

Another point of interest is the difference between the form of the carbon dioxide time curves and those for the other gases. For some reason, possibly because of the small amount of scaling that occurs at these temperatures in carbon dioxide, the scaling rate is approximately constant at least up to 5 hours exposure. This may possibly indicate that certain thicknesses of scale are necessary before the diffusional character of the scaling process becomes apparent by decreasing the scaling rate as time increases. The remaining curves in this series exhibit nicely the diffusional mechanism of scaling in that such a mechanism requires decreasing rates of oxidation with increasing thicknesses of scale which of course will occur with increasing time.

Effect of Variation of Partial Pressure. The data obtained when the partial pressures of carbon dioxide, oxygen and water vapor in mixtures with nitrogen were varied, are summarized in Fig. 7. Oxygen and carbon dioxide show the greatest rate of decrease with decreasing partial pressure below 30 per cent. The scaling losses in the case of steam however fall off very uniformly between 80 per cent and 10 per cent steam. The curves presented in this figure are compatible with the diffusional process which, of course, demands that decreasing the partial pressure of an oxidizing gas, decrease the scaling losses because of the decrease in supply of oxidizing agent to the active surface.

Scaling in Complex Mixtures

Before studying the oxidation of steel in gas-air combustion atmosphere a series of tests was made in which various proportions of carbon dioxide and water vapor were used. The preliminary investigation of scaling in gas-air combustion atmospheres was made by observing the scaling losses occurring in such atmospheres when

various ratios of air to gas were used at four different temperatures in the heat treating range.

Scaling in Mixtures of Carbon Dioxide and Steam

Fig. 8 is a graphical summary of the data obtained when various percentages of water vapor were added to carbon dioxide to form the scaling medium. Scaling is increased in a uniform manner as the water vapor content increases until the atmosphere contains 60 per

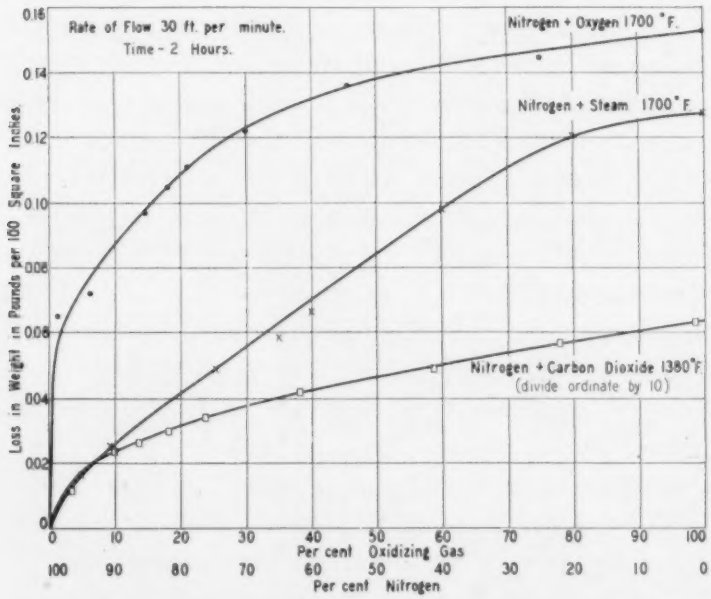


Fig. 7—Effect of Variation of Partial Pressure of Oxidizing Gas on the Scaling of S. A. E. 1015 Steel.

cent steam beyond which the increase in scaling losses brought about by increasing the water vapor content becomes rather small. Scaling in a mixture consisting of 80 per cent steam and 20 per cent carbon dioxide is as great as that in pure steam. This curve shows clearly that changes in the water vapor content of a combustion atmosphere have a very decided bearing upon the results obtained. Therefore slight changes in the original fuel gas composition may so alter the proportion among the various constituents of the products of combustion that decidedly different results may be obtained at the same gas-air ratio.

The curve of Fig. 9 showing chemical composition of the scale as affected by mixtures of carbon dioxide and steam shows a variation

from about 58 per cent to 65 per cent ferrous iron when the carbon dioxide varies from 100 to 80 per cent. The changes in composition over the remaining portion of the curve are not extremely large and show only a gradual transition to the ferrous iron content of pure steam scales. This curve indicates that no marked change in chemical composition of the scale is to be expected in the various gas-air combustion atmospheres where water vapor and carbon dioxide are the only oxidizing gases present.

Scaling in Gas-Air Combustion Atmospheres

Fig. 10 summarizes the data obtained when S.A.E. 1015 steel was subjected to various gas-air atmospheres containing from 0 to 17 per cent carbon monoxide at 1500, 1600, 1700 and 1900 degrees

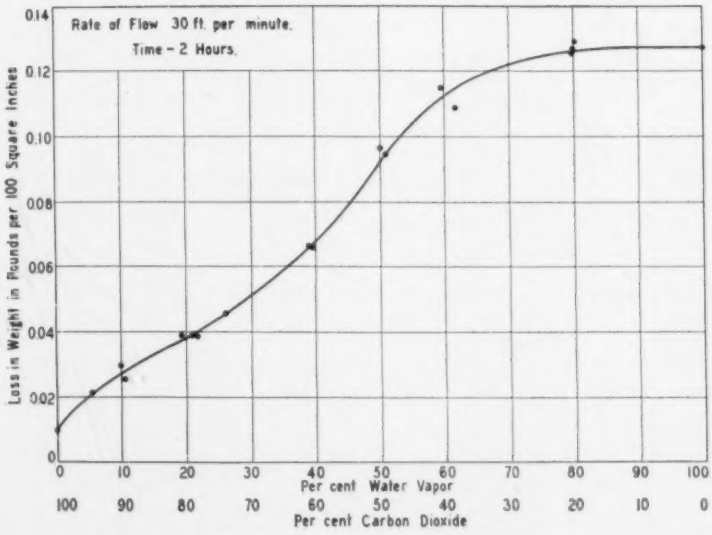


Fig. 8—Effect of Mixtures of Water Vapor and Carbon Dioxide on the Scaling of S. A. E. 1015 Steel.

Fahr. (815, 870, 925 and 1040 degrees Cent.). The curves for 1500, 1600 and 1700 degrees Fahr. (815, 870 and 925 degrees Cent.) show only a slight decrease in scaling losses as the carbon monoxide is increased from 4 to 17 per cent. The 1900 degrees Fahr. (1040 degrees Cent.) curve is considerably higher than the 1700 degrees Fahr. (925 degrees Cent.) curve which would be expected from the characteristics of the temperature curves of the oxidizing gases, Fig. 3, steam and carbon dioxide. Furthermore this curve shows that the scaling losses decrease uniformly as the carbon monoxide is in-

creased from 0 to 12 per cent which was not the case at other temperatures. As the temperature of exposure to gas-air combustion atmospheres is increased the curves show that small amounts, up to 4 per cent, of carbon monoxide have a decreasing influence on the scaling loss.

For temperatures up to 1700 degrees Fahr. (925 degrees Cent.)

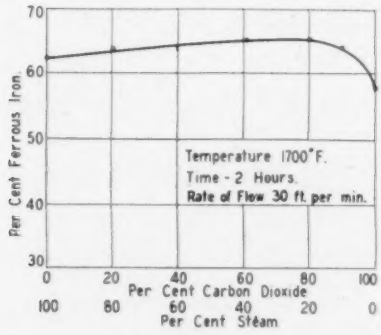


Fig. 9—Variation of Chemical Composition of Scale in Mixtures of Steam and Carbon Dioxide.

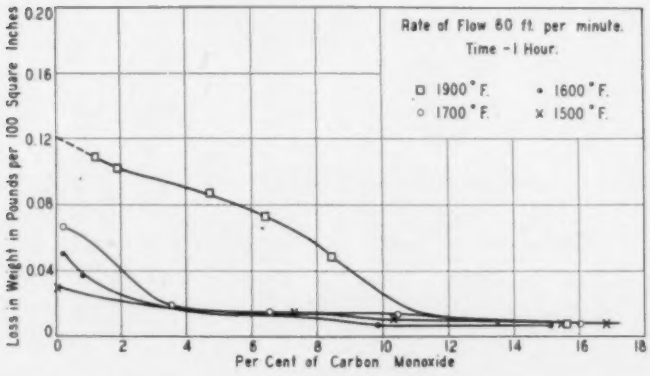


Fig. 10—Scaling of S. A. E. 1015 Steel in Different City Gas-Air Combustion Atmospheres.

scaling losses can evidently be decreased markedly by the use of atmospheres containing 3 to 4 per cent carbon monoxide corresponding to gas-air ratios varying from 1 gas to 4.5 air to 1 gas to 4 air. At a temperature of 1900 degrees Fahr. (1040 degrees Cent.) a 50 per cent reduction in scaling is attained with an atmosphere containing 7 per cent carbon monoxide while 12 per cent carbon monoxide decreases the scaling losses about 80 or 90 per cent. Depending on the work such large excesses of gas might or might not be economical. Increasing the temperature 200 degrees Fahr. in atmospheres

containing no carbon monoxide nearly doubles the scaling losses which indicates that when operating furnaces with such atmospheres unnecessarily high temperatures are to be avoided if scaling is to be kept as low as possible.

Summary

During the course of the presentation of results various theories have been advanced and certain conclusions drawn. These may be briefly summarized as follows:

1. Increasing the velocity of the gas stream in the region below 5 feet per minute, except in the case of oxygen, increases the scaling losses. Above 5 feet per minute velocity has little effect upon scaling losses. In the case of oxygen velocity has very little influence on scaling losses in any region.

2. Below 1300 degrees Fahr. (705 degrees Cent.) there is little difference in the scaling action of steam, carbon dioxide, oxygen and air. From 1300 to 1680 degrees Fahr. (705-915 degrees Cent.) water vapor is the most active oxidizing gas. From 1680 to 1980 degrees Fahr. (915-1080 degrees Cent.) oxygen is most active and above 1980 degrees Fahr. steam again becomes the most active. Air is more vigorous in scaling steel than is steam in the region 1720 to 1850 degrees Fahr. (935-1010 degrees Cent.). Carbon dioxide for the most part is less powerful than any of the other oxidizing gases.

3. The carbon dioxide temperature curve shows a maximum in the neighborhood of 1400 degrees Fahr. (760 degrees Cent.) and a minimum near 1500 degrees Fahr. (815 degrees Cent.). The air curve shows a maximum at 1800 degrees Fahr. (985 degrees Cent.) and a minimum at 2000 degrees Fahr. (1095 degrees Cent.). The oxygen curve shows a change of slope at 1800 degrees Fahr. (985 degrees Cent.).

4. Blistering was first noticeable at 1800 degrees Fahr. in air and oxygen and the decrease in rate of scaling observed in these curves at this temperature is attributed to blistering. This phenomenon may be explained on the basis of Pfeil's hypothesis concerning the inward diffusion of oxygen and the outward diffusion of iron. Blistering above 2000 degrees Fahr. (1095 degrees Cent.) apparently either does not occur or has but little influence on scaling rates.

5. The composition of the scale with respect to ferrous iron shows practically the same effects upon variation of temperature as

do the scaling losses. Minima are characterized by low ferrous iron and maxima by high.

6. Increasing time increases the scaling losses but does so at a decreasing rate except in the case of carbon dioxide. Carbon dioxide shows a practically constant rate of scaling.

7. Decreasing the partial pressure of oxygen, steam, or carbon dioxide by mixture with nitrogen decreases scaling losses.

8. Adding water vapor in increasing amounts to carbon dioxide increases scaling losses until the atmosphere contains about 80 per cent water vapor, after which there is no marked increase.

9. For temperatures up to 1700 degrees Fahr. (925 degrees Cent.) gas-air combustion atmospheres show only a slight decrease in scaling losses as the carbon monoxide is increased from 4 to 17 per cent. The decrease in scaling from 0 to 4 per cent carbon monoxide is quite decided, amounting to 50 per cent or better.

10. At higher temperatures scaling losses are decreased rather uniformly by increasing the carbon monoxide content from 0 to 12 per cent and beyond this very slowly.

11. Up to 1700 degrees Fahr. (925 degrees Cent.) furnaces operating with 3 to 4 per cent carbon monoxide should produce very little scale.

Acknowledgment

The authors desire to express their appreciation to the Committee on Industrial Gas Research of the American Gas Association whose generous financial support has made this study possible. They also desire to acknowledge the aid of N. F. Miller in conducting the many tests connected with this study.

DISCUSSION

Written Discussion: By H. H. Ashdown, metallurgist, Westinghouse Electric and Manufacturing Company, East Pittsburgh.

This paper under review and that submitted by one of the present authors and his collaborators presented before this society at the Boston convention are deserving of careful thought and attention by all steel mill executives. For far too long a period of years it has been taken for granted that scale must be incidental to the process of heating at elevated temperatures.

Until recent years, comparatively little attention has been given to the enormous financial losses resulting from the loss of steel and subsequent heavy costs in descaling for the production of good finished surfaces on cold-rolled sheet, strip and bar stock, in addition to which also must be added the heavy expenditure on cutting tools, etc., when machining badly scaled materials,

particularly forgings of the heavy types which have scale deeply embedded in their surfaces. Again, in the high carbon and chromium alloy steels, where the rate of scaling is more rapid and in the latter case more difficult to remove, the loss and expense are relatively greater. Further, additional heavy losses are incurred in the engineering shops and heat treatment departments where stock has to be machined to remove the decarburized surfaces and when only partially removed, tools during subsequent heat treatment crack, distort or give nonuniform hardness on wearing surfaces. From these reasons alone the authors, for focusing attention on them have rendered the steel industry a valuable service.

There are a number of phases in this paper which offer wide scope for consideration and discussion. In the lower range of heats, say up to 1600 degrees Fahr., which would cover the heat treatment on a wide range of steels for annealing or quenching treatments, it is questionable whether the controlled furnace atmospheres, by dilution of the active gases and retarding combustion would not slow down the rate of heat penetration and under those conditions the restricted rate of output may offset the saving due to actual oxidation. The subsequent losses, however, already referred to must not be lost sight of.

Electrically heated furnaces as commercial units are being rapidly developed and installed in plants for bright annealing and again for more general heat applications where the heat input can be, at any desired rate, and at the same time any desired reducing or neutral atmosphere maintained so that under these conditions production is not restricted and scaling reduced to a minimum.

For the higher temperature ranges such as may be employed for the heat treatment of some of the stainless steels and forgings generally it would, from the authors' paper appear that considerable economic advantage might be gained by soaking the materials between 1800 and 2000 degrees Fahr. both during initial heating or during any enforced holding periods where the scaling rate is at its minimum and subsequently rapidly raising the temperature to the desired forging heat.

On reference to the curves in Fig. 2, one surprising feature is the low and constant rate of oxidation in an atmosphere of oxygen when compared with air under increasing velocity. Although this is again borne out in Fig. 6 on the time-temperature curves, one would almost expect a reversal of those curves due to the diluting influence of the nitrogen in the air atmosphere.

The curves in Fig. 3 also are of great interest, showing the abrupt arrest of oxidation at 1800 degrees Fahr., which the authors well define as being the transition point of FeO to Fe_2O_3. In this connection I would ask the authors if they have noted any marked difference in the readiness of the scale to leave the material in the form of either FeO or Fe_2O_3 or at the transition point around 1800 degrees Fahr. The knowledge of a free method of descaling such as indicated would be invaluable to the steel mills.

There are many other economical advantages which are deserving of close study and practical application, such as furnace atmospheres, pressure and heat flow, all of which would involve considerable discussion, but which, in most cases, can be carefully thought out and applied with good effect.

I would again express my personal appreciation of the value of this paper.

Written Discussion: By O. W. McMullan, metallurgical department, Timken-Detroit Axle Co., Detroit.

This paper is one of practical interest to every heat treater of steel. A comparison of the curves in Fig. 3 for carbon dioxide and air shows the tendency toward much greater scale loss with excess air from improper burner operation above 1500 degrees Fahr. The use of air as a cooling medium to hasten certain annealing operations from 1700 or 1800 degrees Fahr. to around 1300 degrees Fahr. can be expected to show much greater scale loss than that occurring from ordinary combustion gases. Fig. 10 shows that carbon monoxide is apparently more effective in reducing scale loss than in preventing decarburization; around 17 per cent having been reported as necessary for the latter. (Winter in *Metal Progress,* Sept., 1931)

Might not the greater specific volume of Fe_3O_4, together with its lower iron content, give a thicker scale and therefore greater protection for the same iron loss? The explanation of protection by blistering is an interesting one and the writer would like to ask if any observations have been made of loss from purposely produced fluffy scales. This is quite commonly done by dipping in dilute HCl before hardening. No checks have been made of the actual loss, but the scale appears as thick as ever but looser and much more readily removed. Reduction in scale loss might be accomplished by some such method. A blistered surface in such cases as unground gear teeth would, however, be a greater disadvantage than a greater uniform loss because of lapping difficulties and resulting noise.

Written Discussion: By W. E. Jominy, Research Laboratories, A. O. Smith Corporation, Milwaukee.

This paper contains much useful information which can be applied in industry and will bear careful studying on the part of those who heat steel in the range from 1000 to 2000 degrees Fahr. The authors are to be congratulated.

Of particular interest to industry are the results showing the amount of scale produced in various gas-air combustion atmospheres. It appears that at 1500 degrees Fahr. very little reduction in scaling rate occurs in city gas-air combustion atmospheres when the carbon monoxide content is increased from 0 to 16 per cent, and from the nature of the curves it seems a safe assumption that this would be true for temperatures below 1500 degrees Fahr. The question which comes to my mind is whether there is a sharp increase in the scaling rate if a small amount of free oxygen should be present, as is the case at forging temperatures. As is well known, in operating a gas-fired furnace for best fuel economy, it is desirable to maintain an atmosphere as nearly free from carbon monoxide and oxygen as possible. The atmosphere of a furnace so fired, however, will often contain a small amount of either gas (carbon monoxide or oxygen) and, for this reason, it would be very helpful to know whether good scaling resistance would still exist with a small amount of free oxygen, say, 1 per cent, in the atmosphere.

An additional reason for wishing to maintain a furnace atmosphere with no oxygen or carbon monoxide is the decided decrease in decarburization in such an atmosphere compared with that in one containing 2 per cent carbon

monoxide. In the case of decarburization, a small excess of free oxygen has a slightly favorable effect, but an increase in carbon monoxide percentage over one per cent and up to 15 per cent causes an increase in the depth of decarburization at temperatures in the range of 1400 to 1600 degrees Fahr. Of course, my tests on decarburization were carried out on high carbon steels which might behave differently in their scaling reactions than the S.A.E. 1015 steel used by the authors. Have the authors any data on the behavior of the high carbon steels in gas-air combustion atmospheres?

The curves showing the effect of variation of temperature on the scaling rate in air and oxygen are quite surprising. The finding that the decrease in scaling rate at increasing temperature corresponds with decrease in ferrous iron content of the scale suggests that perhaps other steels will behave differently. At forging temperatures it was observed that scale produced in air from high carbon steels contained more ferrous iron than that produced from low carbon steels. If the carbon content of the steel affects the ferrous iron content of the scale, it seems logical that it may also affect the points at which the change in rate of scaling occur, or possibly eliminate them. I hope the authors will find time to investigate this point if they have not already done so.

Another point of importance in connection with scaling is the adherence of the scale to the piece. Certain types of scale seem to shed completely during quenching while others adhere very tightly. This is especially true of oil quenching. The tightly adhering scale not only causes soft spots but difficulty in its removal after quenching, so that usually a thicker, easily-removed scale is preferred to a thin, tightly-adherent one. So far as I know, there are no accurate data available on this subject, and I wonder whether the authors have made any observations of this phenomenon.

SAM TOUR:[1] The authors are to be congratulated for a very interesting paper, indeed. They have given us considerable detailed data that will be of use in time to come. I would like to point out, however, that all of their work has been done on S.A.E. 1020 steel, which is not the steel which many of us heat treat so much. I would like to know if they can tell us whether these same curves are applicable to 1 per cent carbon tool steel, to a 0.50 per cent carbon alloy steel, etc. I do not think that they are.

Again, one of the important things to consider in heat treating work, especially on carbon tool steels, is not the question of scaling so much as it is the question of decarburization. We often think of scaling and decarburization as being connected, but that is not necessarily so.

The main problem in an oil hardening type of tool steel is the problem of soft skin or decarburization. If we were to go by these curves, we would come to the conclusion that such a steel is best heated in an atmosphere containing a certain percentage of carbon monoxide.

Actual tests in controlled atmosphere furnaces of the "Certain Curtain" type have indicated that the oil hardening type of tool steels being heat treated at a temperature of around 1500 degrees Fahr. will come out with a soft skin if an atmosphere containing carbon monoxide is used.

A tool full hard to the surface with no soft skin results when the atmos-

[1]Vice-president, Lucius Pitkin, Inc., New York City.

phere in which it is heated contains somewhere in the neighborhood of 3 per cent of oxygen, 10 to 12 per cent of carbon dioxide and no carbon monoxide. That is not something that you could deduce from the curves which the authors have shown, and I would like to see the authors repeat their work, using oil hardening tool steel and plain carbon water hardening tool steel.

One point which should be brought out is the very active properties of traces of sulphur gases in the furnace atmosphere.

In the heat treatment of stainless steel, for example, traces of sulphur gases seem to cause decided scaling at temperatures around 1800 degrees Fahr.

We have found that sulphur in cutting oils, etc., remaining on the work caused scaling of stainless steel. At 1800 degrees Fahr. this steel heat treats nicely without scaling, in an atmosphere containing 10 per cent oxygen, if it is kept thoroughly clean of sulphur carrying oils and if the gases do not have sulphur in them.

R. J. COWAN:[2] The authors of this paper have given us a lot of additional information regarding the effect of atmospheres on metal surfaces. We can never have too much information of this kind, especially when it is obtained by careful experimentation under definitely controlled conditions. The authors are to be congratulated on this fine piece of work.

One point which should be brought out is the very active properties of tion to the reaction that takes place between carbon and carbon dioxide in the furnace atmosphere, and has suggested the use of a carburizing compound for that purpose. A very satisfactory way to introduce carbon is by means of a gaseous atmosphere. By this means, a very definite control can be maintained and very satisfactory results produced. A very successful development has been carried on along this line, and I believe it is quite in harmony with what our attention has been called to, especially the reaction between carbon and carbon dioxide. By such a means it is possible to raise the temperature of metal to well over 2000 degrees Fahr. without scaling the work. This is being done regularly, and while it is a sidelight on the work that the authors have done in connection with gas atmospheres, I believe it is along the right line, and represents an attempt by industry to approximate as closely as possible the ideal conditions outlined by the authors.

N. E. WOLDMAN:[3] The authors should be highly complimented for their great contribution to our much needed knowledge on the subject of scaling of steel at heat treating temperatures. Such contributions added to the researches on the bright annealing of steels will soon eliminate the worries and trouble of the practical heat treaters and metallurgists.

Scaling of steel has six harmful effects:

(a) It causes nonuniform hardness and produces soft spots in quenching from the hardening temperature.

(b) It removes metal from the surface of the heat treated article and necessitates stock allowance in machining.

(c) It frequently necessitates an extra manufacturing operation, such as wire brushing, sand blasting, grinding or pickling, which in itself is costly.

[2]Surface Combustion Corporation, Toledo, Ohio.

[3]Metllurgical engineer, Westinghouse Electric and Manufacturing Co., East Pittsburgh

(d) It causes nonuniform shrinkage of the steel on quenching. Just as the hot steel touches the quenching liquid part of the scale breaks off, but part adheres to the steel in spots. This will cause nonuniform cooling rate and subsequent nonuniform shrinkage or distortion that was not calculated.

(e) The scale falls to the bottom of the quenching tank and may clog the pump circulating system.

(f) In grinding off the scale the grinding wheels tend to become loaded with the scale and tend to burn the ground steel surface with subsequent danger of producing grinding cracks.

There are several ways of decreasing scaling in gas-fired furnaces; namely, by introducing a diluting inert gas with the products of combustion, by regulating the gas-air mixture in the burners so as to produce a neutral or reducing atmosphere, or by drying the air and gas before entering the burners. Drying the air and gas before entering the furnace burners is costly. Introducing a diluting inert gas as nitrogen is also costly. To regulate the burners so as to produce a neutral or reducing atmosphere is undesirable due to the decreased combustion efficiency.

If competitive prices must be met in the sale of the heat treated products, it is very essential that manufacturing costs be kept to the minimum. This means that an economical method must be found to either decrease or entirely eliminate scale formation in the heat treatment of steel products. We have found that in the heat treatment of gears and springs in gas-fired furnaces, scaling can be decreased to a negligible value by placing a layer of spent carburizing compound in front of the hearth behind the furnace doors. The carbon will combine with the oxygen in the furnace to form carbon monoxide and carbon dioxide. Carbon dioxide is unstable and cannot exist at heat treating temperatures due to its reaction with carbon to form carbon at heat treating temperatures due to the reaction $C + CO_2 = 2\ CO$.

Thus a partial atmosphere of carbon monoxide is economically introduced into the furnaces which we have found decreases scaling as much as 50 per cent if not more. The authors point out in their curves that an addition of 0 to 4 per cent carbon monoxide to gas-air combustion atmospheres decreases scaling as much as 50 per cent or better.

By this simple expedient of placing a layer of spent carburizer compound behind the doors of the furnaces we have eliminated soft spots and have been able to obtain a uniform hardness in hardening pinions, gears and springs.

Authors' Closure

Mr. Ashdown has suggested the possibility of utilizing the reversed rate of scaling in the temperature range 1800 to 2000 degrees Fahr. as a means of minimizing scaling in handling of certain steels. The reversal, which is shown in Fig. 3, is as far as we know limited to an air atmosphere and has been checked only for the low carbon steel. There seems little possibilty however that similar reversals should be expected in combustion atmospheres carrying at most only small percentages of oxygen. The reversal indicated for air and the retardation observed for oxygen, as compared to the rather constant rate of increase in scaling for water vapor and carbon dioxide over the same temperature have, it is believed, a definite bearing on the mechanism

of blistering. It is not the intention of the authors to indicate 1800 degrees Fahr. as a transition point of FeO to Fe_2O_3 but rather as a point at which increasing proportions of Fe_2O_3 are formed. Studies of the percentages of scale retained on quenching have not indicated any great difference in the readiness of the scale to split off at or near 1800 degrees Fahr.

What perhaps appears as a discrepancy in the curves of Fig. 2 for scaling rates of air and oxygen as affected by the rate of flow is explained when one observes that the air curve is for 1700 degrees Fahr. and the oxygen curve for 1520 degrees Fahr. Unfortunately in attempting to reduce the number of figures by using two sets of coordinates, the relative scaling rates are not indicated by the positions of all of the curves of Fig. 6. The ordinate values for the oxygen curve at 1520 degrees Fahr. are to be multiplied by 10. The diluting influence of the nitrogen in the air then becomes evident.

Mr. Tour and Mr. McMullan have very properly pointed out that decarburization as well as scaling must be given consideration in any study of the effects of furnace atmosphere. However, in the present investigation, the authors were primarily interested in scaling rather than in decarburization. Jominy had previously reported an investigation of decarburization of steel at heat treating temperatures (Engineering Research Bulletin 18, 1931) which was carried out in these laboratories. In order to avoid the introduction of decarburization effects to any greater degree than was necessary a low carbon steel was chosen for the fundamental or basic part of the investigation. The material presented in this paper has been restricted to this phase of the work and consequently data on the behavior of medium or high carbon steels or alloy steels do not appear. Work, however, has been carried out on these other steels and it is expected that the results will be published in the near future. The importance of sulphur in the furnace atmosphere is appreciated and one phase of this work was reported on by one of the authors at this meeting.[1]

Mr. Jominy has raised a number of questions in connection with the problem of scaling. Some of these questions anticipate results that were obtained in the second part of our program and which were not included in the present paper. This is perhaps to be expected in that the present investigation is an outgrowth of the study of scaling at forging temperatures made by Mr. Jominy and Dr. Murphy. While runs have not been made at 1500 degrees Fahr., tests at 1700 degrees Fahr. indicate that small percentages of free oxygen result in rapid increases in the rate of scaling. Further investigations of the retarded rates of scaling in oxygen and air are being carried out, but so far no information pertaining to the relation of the carbon content of the steel to the ferrous iron content of the scale have been obtained. The authors have no information bearing on Mr. Jominy's suggestion relative to the effect of the quenching medium on the physical character of the scale or to Mr. McMullan's suggestion relative to the effect of pretreatments.

The authors are indebted to Dr. Woldman for his enumeration of the harmful effects of scaling and to both Dr. Woldman and Mr. Cowan for pointing out methods of obtaining the beneficial effects due to the presence of carbon monoxide in the furnace atmosphere.

[1] "Behavior of Steel in Sulphur Containing Atmospheres at Forging Temperatures." Preprint No. 6.

THIN STRIP STEEL FOR DEEP DRAWING

By H. T. Morton and I. A. Rummler

Abstract

In this paper the authors discuss the various tests applied to thin strips of hot and cold-rolled steels used for deep drawing operations. They show that the same kind of tests apply for both steels but the limits are slightly different. Good hot-rolled steel should have a Rockwell hardness, B scale, of 45 to 62 and should not crack, roughen, or break during an 180-degree bend test. Cold-rolled steel should Rockwell B35 to B55, should not crack, roughen, or break in an 180-degree bend test flattened out again, and should have a bright surface free from defects.

Introduction

THIS paper deals with the testing and writing of specifications covering thin strip steel (0.062 inch and under) for deep drawing purposes such as ball and roller bearing retainers, bands, etc. These data are of special interest to the small user of this type of material who is not equipped with an Erichsen or similar cup-forming testing machine and must rely upon more simple methods of testing. The whole purpose in formulating tests of steel is to determine whether the steel will work in a given deep drawing operation without actually setting up the presses to form the parts. Thus a shipment of steel can be tested and accepted upon arrival at the plant without altering the production schedule of the presses for months, if not required in process. It is assumed that the mechanical engineer, toolmaker, and mechanic have overcome the difficulties of die design and machine set-up so that only the testing and the correlation of these results with production results are here considered.

The four types of deep-drawn parts studied are shown in Fig. 1. A is a roller bearing cage; B an angular contact ball bearing retainer; C a thrust bearing band; and D a ball bearing retainer. There are slight differences in the type of material and the test tolerances used

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The authors are members of the Society. H. T. Morton is metallurgist and I. A. Rummler is assistant metallurgist for the Hoover Steel Ball Co., Ann Arbor, Mich. Manuscript received June 8, 1931.

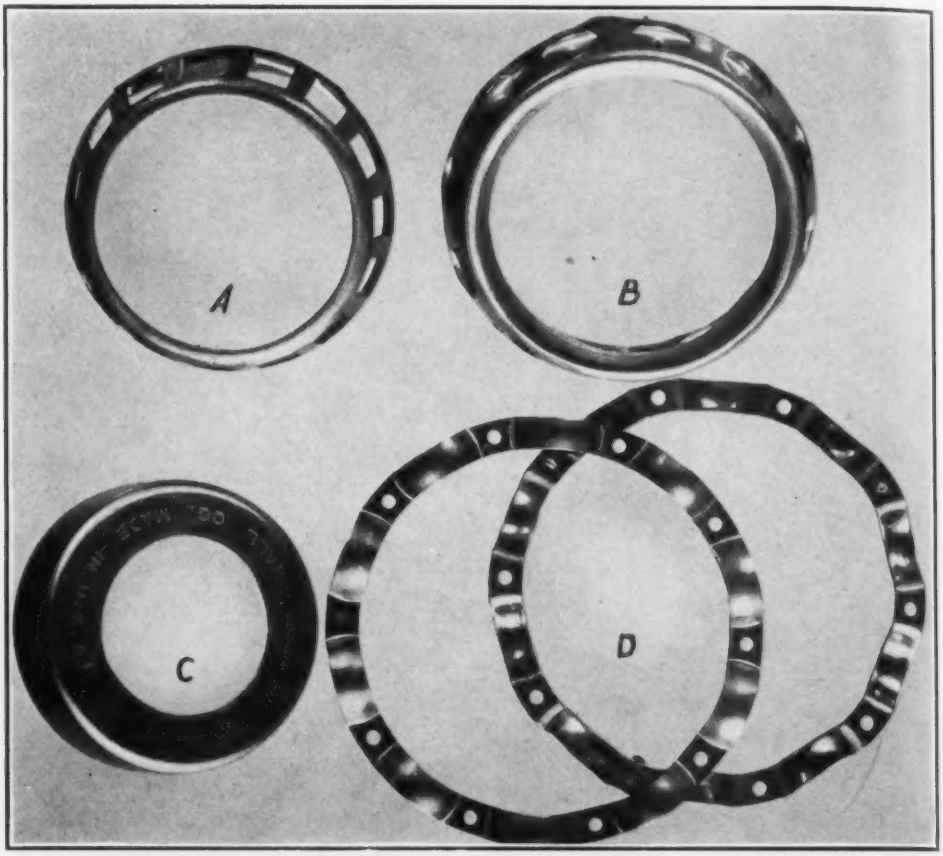


Fig. 1—Formed Parts Considered in this Paper. (A) is Roller Bearing Cage; (B) an Angular Contact Ball Bearing Retainer; (C) a Thrust Bearing Band; (D) a Ball Bearing Retainer. Full Size.

for each but the test methods and principles involved are the same for all. Actual differences will be shown in detail later.

The steel under consideration is purchased in the form of strips varying in thickness from 0.025 to 0.062 inch and in width from 1½ to 5 inches. It is made in large open-hearth furnaces under careful control to eliminate pipes, slag, inclusions, and internal defects. For the roller bearing cages (Fig. 1A) standard hot-rolled steel is used. For all other parts the steel is cold-rolled to size after the regular hot rolling operations, and annealed below the critical temperature to obtain the proper hardness and relieve any rolling strains. Both materials have the following analysis range, corresponding to S.A.E. 1010:

	Per Cent			Per Cent
Carbon	0.05 to 0.15	Phosphorus	under	0.045
Manganese	0.30 to 0.60	Sulphur	under	0.055

This work was first begun five years ago by making laboratory tests on each shipment of steel, keeping it separate through the press operations, and reporting to the laboratory as to results in production. Soon a correlation was found between good production results and the following laboratory tests: Rockwell hardness, B scale; bend tests; microstructure; surface conditions, etc. Without repeating the work chronologically, the types of tests and effects are given.

Rockwell Hardness

This test is of greatest importance in order to get parts of uniform size from the dies, as Rockwell hardness has a direct relation-

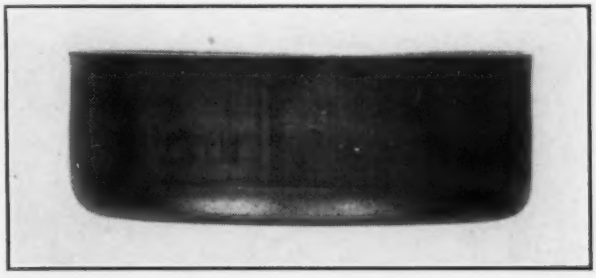


Fig. 2—A Thrust Bearing Band Scratched on the Surface from Metal "loaded-up" on the Die. Natural Size.

ship to the tensile strength, and an increase in the latter tends to cause the parts to flatten out or "spring back" to their original shape after release from the dies.[1] Thus a range of Rockwell hardness, B scale, must be adopted in order to get uniformity of parts from the same shipment or successive shipments.

Production results showed that an increase in hardness beyond certain limits caused cracking of the parts at the edge of the bend with no definite relationship to the dies or the direction of rolling of the steel. A decrease in hardness below certain limits almost eliminated "spring-back" and made the steel "dead," but was detrimental in "loading-up" the dies with metal, thereby causing them to badly scratch parts which were subsequently formed as shown in Fig. 2. Such dies would have to be re-polished as soon as they "loaded up." Several types of lubricating oils have been tested and are effective in decreasing this "loading-up" of metal on the dies.

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[1]W. H. Graves, "Sheet Steels for Automobiles," *Journal*, American Society for Testing Materials, 1930.

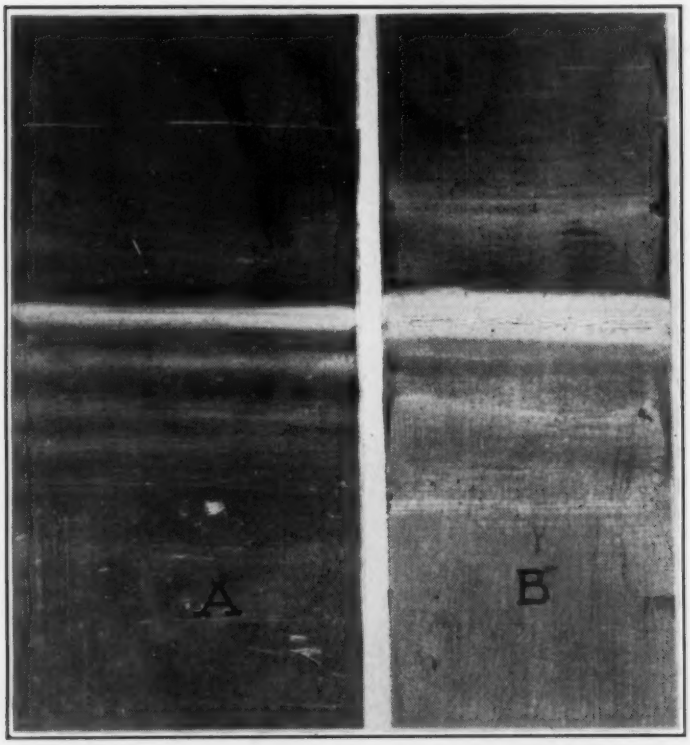


Fig. 3—Bend Test Specimens Flattened Out. The Left (A) is Satisfactory in this Test. The Right (B) is Cracked on the Inner Surface. Natural Size.

Careful comparison of production results with Rockwell hardness values (B scale, 100-kilogram load, $\frac{1}{16}$ inch ball) indicates the following limits are most satisfactory for the parts formed:

Cold-rolled steel	Hot-rolled steel
35 to 55	45 to 62

To obtain these hardness values the cold-rolled steel is given a final low temperature anneal after rolling to correspond to "dead soft" steel, while the hot-rolled steel is finished at proper temperature and slowly cooled without subsequent annealing.

Bend Test

Many of the larger companies employ Erichsen or similar cup-forming testing machines which combine a bend test, hardness test, elongation test, and surface test in one operation. If this equipment is not available, a method of bend testing can be used. Most com-

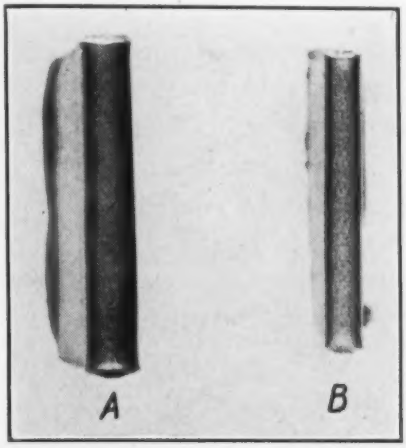


Fig. 4—Bend Test Specimens. The Left (A) is Satisfactory in this Test. The Right (B) is Roughened on the Surface Due to Grain Growth from "Recrystallization." Natural Size.



Fig. 5—Microstructure of a Hot-rolled Strip Badly Decarburized on the Surface. It also Showed Surface Roughening as in Fig. 4. Etched 70 seconds in 2 per cent nital. Magnification × 100.

panies[2] recommend an 180-degree bend of test specimens (6 inches long by 1 inch wide) upon themselves or upon material of equal

[2]"Tentative Specifications for Cold-Rolled Strip Steel," American Society for Testing Materials Designation A 109-27T issued 1926 revised 1927 in American Society for Testing Materials Tentative Standards, October, 1930, page 30.

thickness to the test specimens. Transverse test specimens are 1 inch wide and of length equal to the width of the strips. This method of testing is satisfactory for the hot-rolled steel and requires that neither transverse nor longitudinal specimens break, crack, or show undue roughening of the surface.

For all other parts made of cold-rolled steel the transverse and longitudinal specimens must be bent 180 degrees upon a strip of equal thickness and straightened out flat without causing the inner surface to break, crack, or show undue roughening. At least six (under 0.5 per cent) strips are tested from every shipment. Satisfactory and cracked bend test specimens are shown in Fig. 3. Specimens of typical smooth and rough surfaces are shown in Fig. 4.

Microstructure

Only in cases where trouble is encountered is the steel examined for microstructure. Where the surface roughens during the bend test, the structure (etched 70 seconds in 2 per cent nital) generally shows grain growth. Two causes of this grain growth have been

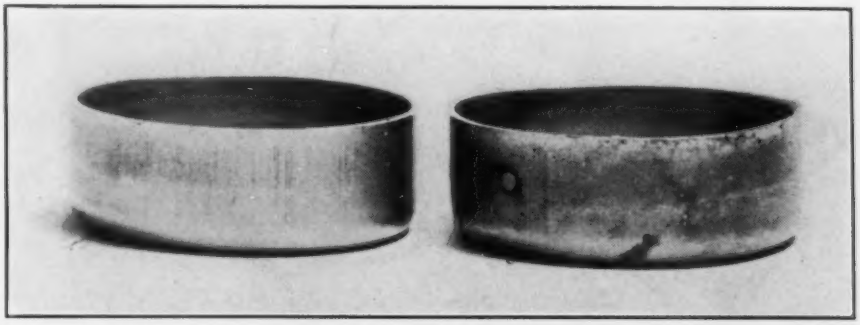


Fig. 6—Two Formed Bands Showing a Good Shear at the Left and an Irregular Shear at the Right, Caused by the Strip Being too Hard or too Thick at its Center Compared to its Edges. Natural Size.

found, namely, decarburization and "recrystallization during annealing of cold-worked steel." A photomicrograph of decarburized structure of hot-rolled steel is shown in Fig. 5. Recrystallization is similar in structure except that instead of the thin boundaries of pearlite, large grains of pearlite are found between the large grains of ferrite.

Irregularity of Edge After Forming

Many formed parts have a smooth enough edge that they can be used without trimming, while others are quite irregular as shown in

Fig. 6. Production results indicate that the latter condition is found more often on parts made from cold-rolled steel than from hot-rolled steel. Two factors were found to increase this irregularity of the edge, namely: having the centers of the strips harder or thicker than the edges. Safe limits for these two items are: maximum variation in Rockwell hardness across a strip, 5 points; maximum variation in thickness across a strip, 0.002 inch.

Surface Conditions

A small percentage of strips from each shipment should be examined for surface conditions, size tolerances, and internal defects to make certain that the finished parts will have the desired bright finish. Such defects may be listed as: dark areas; seams; pipes; handling defects; and variation in tolerance.

Dark areas—These spots may originate from any of several causes, such as: excessive scale on the hot-rolled steel; insufficient pickling; oxidation during annealing; and low spots on the hot-rolled strips. Their effect is to leave an irregular color on the finished parts, not removable without an extra amount of tumbling or added operations. These causes can be corrected by experienced mill operators.

Seams—Seams generally originate in the hot mill and are not removed during the cold rolling. An experienced inspector is needed to find them on rolled strips. Lack of detection weakens the parts and may cause a large number of split or broken parts.

Pipes—The cause and effects of pipes need no comments. Detection can be accomplished by examining the sheared ends of the strips or by bending a short sample cut from the ends of the strips.

Handling defects—Where the quality of the finished parts requires a smooth surface free from dirt, roughness, and uniform in size, the steel must be handled carefully at the mill, in transit, and in production. Slight scratches, pits, laminations, indentations, etc., will pick up dirt and hard gritty material, thereby increasing these defects and causing size and surface irregularities during the forming operations. Sometimes this foreign matter will be imbedded deep enough in the metal to require an added cleaning operation. Thus scratched, rough, or dirty strips and shipments should be cleaned or scrapped to prevent trouble.

Size tolerances—Variations in thickness cause irregularities of the sheared edge of formed parts and such steel must not vary more

than 0.002 inch across a strip. Allowable variation between strips depends upon the limits of the finished parts. Standard mill tolerances apply for most parts, namely:

Widths Thickness (Inch)	Cold-Rolled Steel ½ to 2 Inch	2 to 4 Inch	4 to 6 Inch	Hot-Rolled Steel 3½ inch and under
0.050 to 0.075	±0.002	±0.002	±0.003	±0.004
0.035 to 0.049	±0.002	±0.002	±0.002	.....
0.031 to 0.034	±0.0015	±0.002	±0.002	.....
0.020 to 0.030	±0.0015	±0.0015	±0.002	.....

Specification for Cold-Rolled Steel

All of the parts here discussed can be made from the same type of cold-rolled steel, which would meet the following requirements:

Analysis	S.A.E. 1010
Rockwell hardness, B scale	35 to 55
Rockwell hardness variation	5 points maximum within a strip
180-degree bend, flattened out	No cracks, breaks, or roughening
Structure	Free from grain growth
Surface	Clean and bright
Size tolerance	Standard mill limits, not exceeding 0.002 inch

Specification for Hot-Rolled Steel

Analysis	S.A.E. 1010
Rockwell hardness, B scale	45 to 62
180-degree bend test	No cracks, breaks, or roughening
Structure	Free from grain growth
Surface	Pickled and oiled
Size tolerance	Plus and minus 0.004 inch

Summary

The essential points in this paper can be summarized as follows:

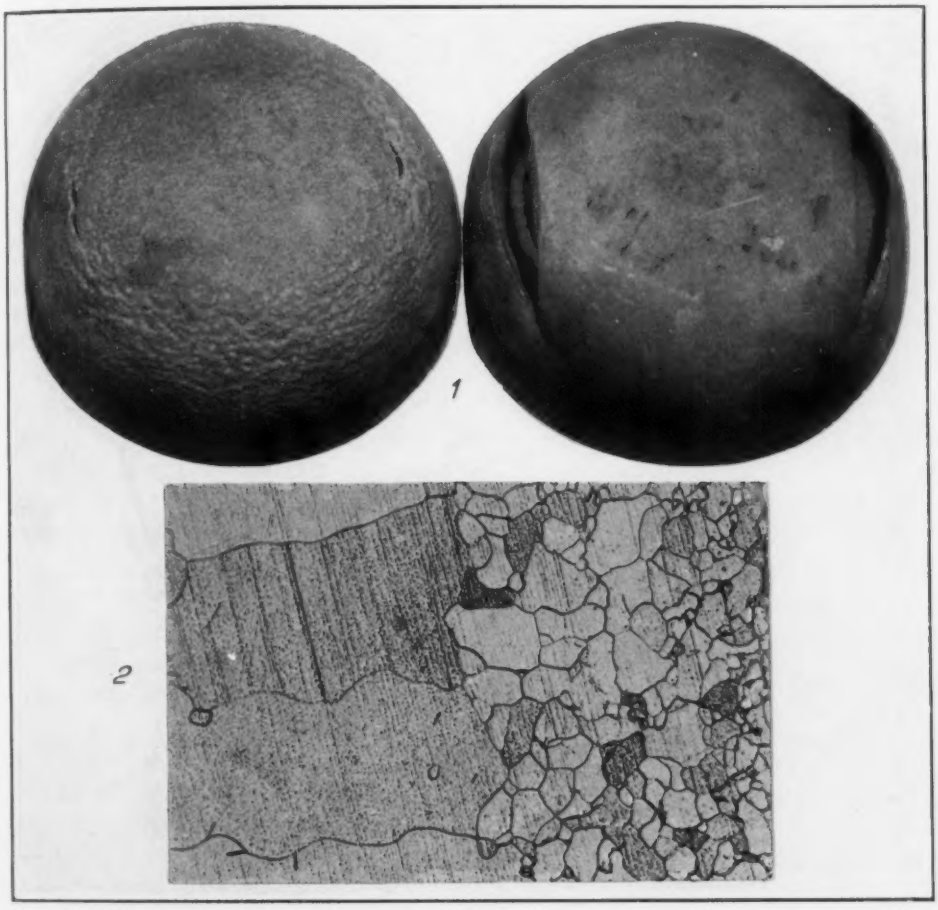
1. Suitability of steel for deep drawing purposes can be determined accurately by laboratory tests.
2. For uniformity of size of formed parts, definite limits of Rockwell hardness must be adopted.
3. Bend tests give accurate information on the drawing quality and structure of this steel.
4. Each strip of steel must be uniform across its surface for hardness and thickness to obtain a smooth edge on parts.
5. Inspection of small percentages of shipments for surface conditions insures uniformity of finished parts.
6. Typical specifications for steels are given.

DISCUSSION

Written Discussion: By L. C. Miller, metallurgist, Republic Steel Corp., Detroit.

We wish to commend the authors of this paper for their thorough investigation and their clear presentation of results obtained. Both have had excellent opportunity to study the problem they have discussed in their paper.

We wish to confine our remarks primarily to that part of the authors'



paper referring to hot-rolled strip. Considerable care by the mill is absolutely necessary in processing either hot or cold-rolled low carbon strip steel in order to insure satisfactory deep drawing qualities, and then correct dies and drawing lubricants must be used by the manufacturer or defective stampings will result.

Regardless of whether the material is alloy or carbon steel, uniformity of analysis is of first importance and, obviously, such defects as pipe and segregation, or surface seams and laps, will probably cause stampings to split. Rather close tolerance size is necessary so that stampings do not bind in the

die, causing tearing of metal, or split dies. Proper lubricant used in the dies is of considerable help in preventing tearing of metal, and even splitting of parts, such as bearing cups.

In particular reference to 0.08 to 0.12 per cent carbon, 0.30 to 0.50 per cent manganese, hot-rolled strip steel, approximately 0.250 inch thick and 3¾ inch wide, intended for cold stamping into bearing cups and then machining into bearing races, we have found that it is necessary to control the analysis as well as rolling and annealing temperatures to insure uniform hardness and structure, and satisfactory deep drawing qualities. If this is not done, splitting of cups or similar parts will occur in the deep drawing, and even machining difficulties may arise.

The authors have referred to a grain growth or recrystallization of decarburized surface on such cups, and have included some photomicrographs showing such conditions. We wish to submit some additional macrographs and photomicrographs which clearly show such decarburized surfaces, which also show extreme grain growth. Cups could not be stamped successfully from such material which may be characterized as having "orange peel" surface. Splitting occurs to a very marked degree in extreme cases. Neither tensile or Rockwell hardness tests revealed this condition.

Fig. 1 is a macrograph of two natural size split cups, one due to light surface seams and one due to decarburized, recrystallized surface or "orange peel." This quite clearly shows the effect both of surface defects and of an excessively coarse-grained decarburized rim 0.035 inch deep.

Fig. 2, at 50 diameters. shows the excessive size of the ferrite grains in the decarburized rim of the same cup as shown in Fig. 1. It also reveals the much smaller grain size below the decarburized zone. Also proper structure below decarburized zone.

Actual analysis of millings proved that the surface was decarburized with only 0.03 per cent carbon present, compared with 0.12 per cent carbon underneath the rim. In addition to cups showing this decarburized rim splitting in forming, this coarse low carbon rim caused tearing in machining and made it difficult to hold dimensions.

Similar conditions could occur in cold-rolled strip as in the hot-rolled product, hence we concur in Messrs. Morton and Rummler's conclusions that uniformity of structure, as well as hardness, is necessary for deep drawing of thin strip steel.

Written Discussion: By R. L. Kenyon, supervising research engineer, American Rolling Mill Co., Middletown, Ohio.

These authors are to be complimented on the willingness they have shown to publish the results of their experience in testing material for various parts used in ball and roller bearing construction. Without detracting from this feature of the paper, it might be well to consider that this is only one deep drawing problem and that, therefore, the results are not necessarily of general application to all deep drawing problems.

It is felt by the writer that while the Rockwell is a good test as far as it goes, it is not entitled to the implicit faith that the authors of this paper seem to place in it. For example, the ranges given for cold-rolled and hot-

rolled steel seem rather wide compared with the experience of others in this field. An accurate tensile test will give more information concerning the behavior of sheet metal than any test we have experimented with. But its results must be interpreted properly or it may be misleading as well as some of the other tests in use. For example, the authors' statement, "Thus a shipment of steel can be tested and accepted upon arrival at the plant without altering the production schedule of the presses for months," implies that the material will show no change in properties during that time. Under certain conditions the drawing qualities may be materially changed, due to the phenomenon of "aging."

The "spring back" mentioned on the third page is more a function of yield point than tensile strength. It is true, however, that material which shows low Rockwell is often low in yield point, as well as tensile strength, so that the Rockwell does give some indication in this case. We have seen cases, however, where slight increase in Rockwell has decreased "spring back."

The irregularity of the edge of drawn cups is attributed by the authors to variation in gage and hardness from center to edge of the strips. Experience has shown that the principal cause of this is nonuniformity of the material in respect of direction. In other words, the strips have "directional properties." This is a fine example of the limitation of hardness or "cupping" tests.

Tensile tests made on such material would show a significant difference in ductility with and across the rolling direction. Tests made at 45 degrees to the rolling direction will show more elongation than any other direction if such directional properties exist in the sheets. This can be further verified by examining the location of the "ears" in the drawn forms, providing they are round. If this is the case, the "ears" will be located at points 45 degrees to the rolling direction.

The first point mentioned in the summary seems to be entirely too general as based on the results presented. In the first place the draws illustrated are not exceptionally difficult and the Rockwell limits given bear this out. As long as the material has good surface, is not coarse-grained, and is rather soft, it should give no trouble for this operation. Such problems as "stretcher straining," for example, are not involved in the draws shown. As a matter of fact, many tests have been made in an effort to correlate the results of physical tests with performance under the dies. With the simple draws shown in this paper this is possible, perhaps, but there seems to be no justification for the general assumption that the same methods will solve all drawing problems. Experience indicates that much more than Rockwell and reverse bending tests will be required.

Authors' Closure

Mr. Miller's comments on finding similar difficulties on parts formed from hot-rolled strip steel, having surface decarburization and seams, are greatly appreciated and confirm the authors' results.

It is agreed with Mr. Kenyon that the Rockwell hardness limits given in the paper are much wider than the range within which a steel mill can hold the various lots of steel. This wide range was given because it was between

these limits that no trouble was encountered from "loading up" of the dies with soft steel or broken parts from hard steel. For the particular parts studied this range of hardness was satisfactory and represented dead soft cold-rolled strip steel. Other manufacturers may find that, in order to get their size uniformity their hardness variation will have to be narrowed to a 10 point range, B scale, which might also require narrowing their carbon content to an 0.05 per cent range.

Changes in hardness of steel due to "aging" seem to occur more rapidly in steel which has had a finish rolling operation after annealing rather than on fully annealed steel. If this is so, subsequent hardness changes from aging this dead soft steel will have a negligible effect on the Rockwell hardness and deep drawing results, especially on these particular parts.

In the cups formed from strips having a variation in thickness or Rockwell hardness, it was found that the "ears" come in the direction of rolling rather than at 45 degrees to this direction, as pointed out by Mr. Kenyon. A theory of this cause comes from the tendency of the steel to equalize in thickness, due to the equal clearance between the die and punch, thereby causing the surplus material to be drawn out in the form of "ears" at the strip ends. Probably the difference in hardness in the centers of the strips was caused by greater compression of the strips, due to the crown effect in the hot-rolled strips. If so, the forming operation tends to allow this metal to expand to its original thickness, but due to lack of die and punch clearance, it is lengthened instead to form the "ears."

It is admitted that the formed parts discussed in this paper are not the most difficult ones to make, but laboratory tests are satisfactory in determining whether the steel will work on this production. Similarly these tests or others which might be added can determine the quality of steels for other deep drawing applications without requiring actual production operations, provided there is proper co-operation between the steel producer, laboratory control, and production men.

SOME EFFECTS OF THE AMOUNT AND RATE OF DEFORMATION ON A LOW CARBON STRIP STEEL

By Joseph Winlock and Alfonso E. Lavergne

Abstract

This paper gives the results of some experiments which show some effects of the amount and rate of deformation on a low carbon strip steel. "Lines of Lüder" (stretcher strains) and their formation are described.

ONE of the greatest difficulties encountered in the forming of sheet and strip steel by the deep drawing process is the occurrence of "stretcher strains" on the surface of the metal after the draw has been completed. Stretcher strains or, more appropriately, "worms" are the shop names for the phenomenon known as the "Lines of Lüder" after Lüder of Magdeburg, who first described them in 1860.[1] These lines appear on the surfaces of the metal after drawing as irregular lines of depressions or elevations which destroy the evenness of the surfaces of the metal. If the stresses producing the deformation are primarily tensile, the lines appear as depressions in the surface; but if the stresses are primarily compressive, irregular lines of elevations occur. They tend to occur in those stampings or parts of stampings in which the elongation in forming is between 1.5 and 10.0 per cent. Sometimes these markings are so extensive that it is necessary to grind and polish the entire surface of the stamping (see Fig. 1). Even this is not always accomplished satisfactorily because the heat produced by these operations tends to cause a severe distortion of the stamping.

In a paper presented before this society in February 1930,[2] with one of the present authors as co-author, stretcher strains were described as being due to the fluctuations occurring at the yield point by the transitions in different grains or groups of grains from the

[1]Dingler's Polytechnisches Journal. 1860. Vol. 156, p. 18.

[2]Joseph Winlock and G. L. Kelley, "Sheet Steel and Strip Steel for Automobile Bodies," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 254.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. Of the authors, Joseph Winlock, a member of the society, is metallurgist and Alfonso E. Lavergne is associated in an engineering capacity with the Edw. G. Budd Manufacturing Company, Philadelphia. Manuscript received July 22, 1931.



Fig 1—Photograph of a Stamping Showing Stretcher Strains.

elastic to the semi-plastic state (see Fig. 2) and that severe surface markings could occur only in those metals in which this transition were relatively abrupt. It was pointed out that the surface markings decreased in magnitude as the load (produced by the increasing deformation) increased until the effect of contrast was so diminished as to effect a return to the original even surface. It was shown that by properly regulating the amount of cold work performed on the steel prior to the deep drawing operation, the stress-strain diagram could be made relatively smooth from origin to fracture (see Fig. 3). Such treatment prevents the occurrence of stretcher strains in the stampings, provided, of course, that before the deep drawing operation, there has not been time enough for the return of elasticity ("aging") to take place.

In an attempt to throw some further light on Lüder line formation, we have just completed a few experiments which, although preliminary, nevertheless gave such interesting results that we felt it might not be out of place to report them at this time.

Tensile specimens were machined from a sheet of strip steel (0.037 inch in thickness by 36 inches wide by 97 inches long) which had been made according to regular mill practice, i. e., hot-rolled from a slab to about 0.060 inch in thickness, annealed and reduced by cold rolling to 0.037 inch in thickness, and finally box-annealed at 1400 degrees Fahr. (760 degrees Cent.). The specimens were taken in directions both longitudinal and transverse to the direction of rolling. They were 0.750 inch in width and the gage length used was 8 inches. They were divided into two lots; one lot for testing without further treatment and one lot to be heated before testing to above the Ac_3 point of the steel. The latter were carefully sealed in pipes to prevent scaling, placed in a furnace which had been heated to 1750 degrees Fahr. (950 degrees Cent.), held for three hours, and then drawn from the furnace and allowed to cool in the air.

The chemical analysis of the steel was: carbon, 0.06 per cent; manganese, 0.36 per cent; phosphorus, less than 0.015 per cent; and sulphur, 0.030 per cent. The percentage elongation in 8 inches in both steels when tested in the usual manner at a rate of deformation of 2 inches per minute was approximately the same; namely, 31 per cent. The specimens were then pulled at the following different rates of deformation; 2, 9.5, 10, 14.5, 16, 18, 19, 22, 39, 60, 96, 102, 126, 156 and 252 inches per minute.

In pulling the specimens annealed at 1400 degrees Fahr. (760 degrees Cent.), it was found that when the rate of deformation increased to 19 inches per minute the irregular lines of depressions did not "widen" and "disappear" in every test piece, but that fracture occurred before parts of the specimen had permanently elongated. An average of four longitudinal and four transverse specimens were pulled at each rate of deformation. Premature fracture occurred

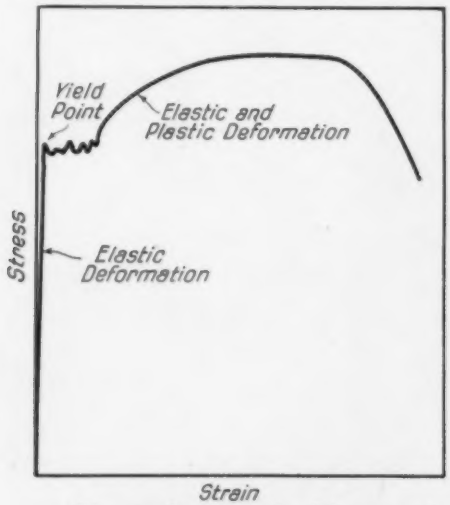


Fig. 2—Stress-Strain Diagram of Steel Specimen.

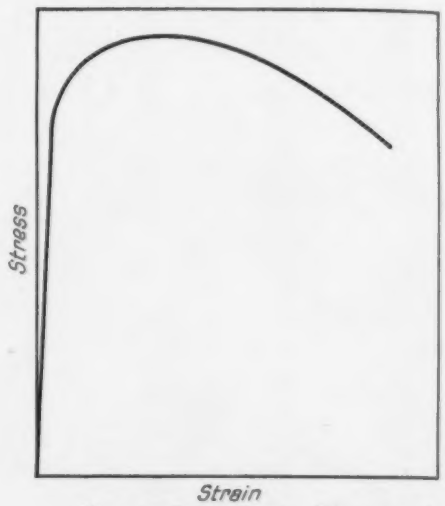


Fig. 3—Stress-Strain Diagram of a Steel Which Has Been Cold Worked and Immediately Permanently Deformed.

in at least five out of each eight tests when the rate of deformation exceeded 19 inches per minute. When premature fracture occurred, the percentage elongation in 8 inches was, of course, very low because only parts of the specimen had elongated. Fig. 4 shows two specimens which fractured in this manner and Fig. 5 shows a portion of such a specimen.

The specimens which had been heated to 1750 degrees Fahr. (950 degrees Cent.) were pulled at the same rates of deformation. Stretcher strains formed as usual, but in every case these "widened" and "disappeared" as the deformation increased. In no case did premature fracture occur.

Specimens of the steel annealed at 1400 degrees Fahr. (760 degrees Cent.) were then pulled at a rate of 2 inches per minute until all of the large depressions had "appeared" and "disappeared." An elongation of 10.0 per cent was necessary to do this. The test pieces were then immediately (so that very little aging could occur) elongated to fracture at a speed which would have yielded a low

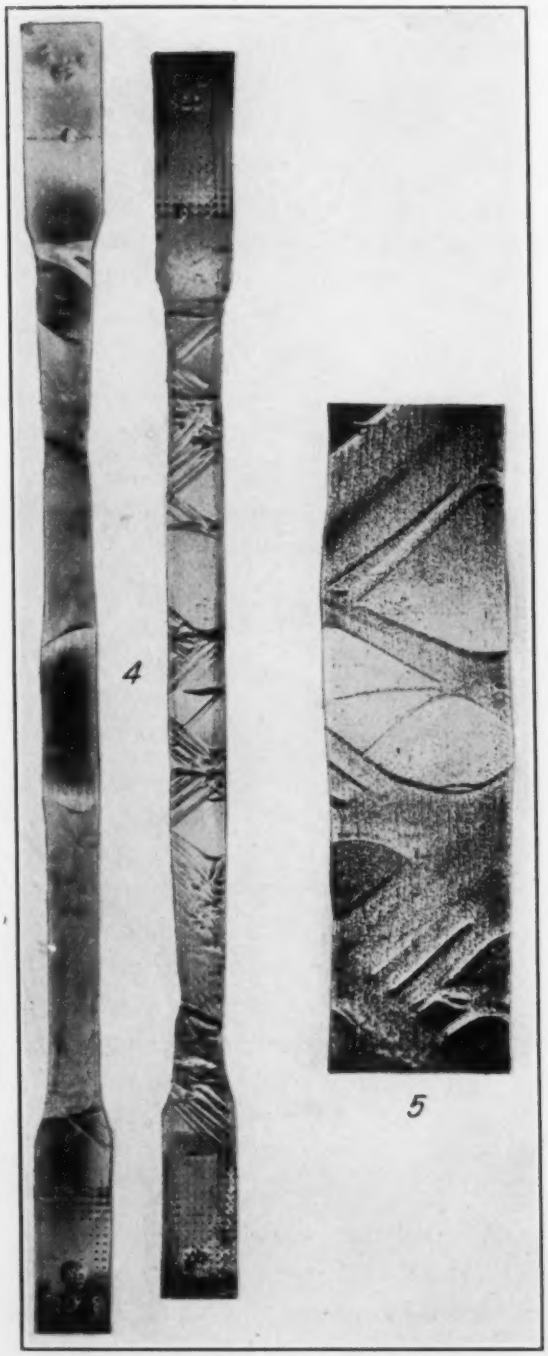


Fig. 4—Photograph of Tensile Specimens Showing Unstretched Portions After Fracture.
Fig. 5—Photograph of a Portion of Broken Tensile Specimen Showing Unstretched Portions After Fracture.

percentage elongation and would have left portions of the steel unstretched had this speed been used alone: 252 inches per minute. It was found by first employing this slow speed followed immediately by the faster speed that the detrimental effects of the fast rate of deformation were removed: premature fracture did not occur in any case.

Without attempting to explain the underlying causes, a brief discussion is offered of some of the results obtained. The permanent deformation of steel takes place by the alternate slipping and work-strengthening of the different grains or groups of grains. When the load induced by the deformation reaches the yield point of the steel, the resistance to permanent deformation is overcome and slip commences. The intensity of the stress on the grains which yield first is increased by virtue of the reduction in cross sectional area, but due to work-strengthening, the resistance to further slip is also increased. The result of this is that the actual load-carrying capacity of the permanently deformed grains becomes greater than that of their only elastically (or semi-plastically when the extension has become greater) deformed neighbors. It is obviously fortunate that this is so, otherwise steel could not be formed by the deep drawing process, because if the metal behaved as a perfectly plastic material, the slightest concentration of the imposed stress (caused perhaps by the shape of the finished article) would cause fracture to take place. Pitch, for example, could not be drawn because no work-strengthening would take place at the point at which the cross sectional area is first reduced. Fracture would result almost immediately. In order to shape a perfectly plastic material by the deep drawing process, then, it would be necessary to have (1) a perfectly homogeneous substance, and (2) an absolutely uniform distribution of the stress. These are two conditions which would be very difficult, if not impossible, to obtain.

In the ordinary tensile test, the rate of deformation of the specimen as a whole is constant while the load varies according to the resistance to the deformation set up by the steel. Stress-strain diagrams obtained under these conditions show beyond the yield point only the average elongation and the actual total loads induced by the deformation. Thus, if after a portion of the specimen has slipped, the gage length were to be shortened so that only this portion of the specimen were included, the stress-strain curve would be found to be rising as a comparatively smooth curve. This small gage length

usually does not in itself show any severe surface markings. If, however, the longer gage length is considered, it is found that a difference in level exists between the portions which have slipped and those which have not slipped. It is the effect of this contrast which produces the severe surface markings. We do not mean to infer that the small gage length does not show some markings, too, but we find that these are usually so small as to be almost indistinguishable. Contrast is a question of degree and not kind.

The actual increase in resistance to slip, resulting from the permanent deformation of steel, is, however, not only dependent upon the amount of permanent deformation and the temperature at which it is performed, but also upon the *rate at* which the deformation is produced. Numerous and large differences in resistance to permanent deformation would tend to accentuate these conditions.

By pulling the specimens heated to 1400 degrees Fahr. (760 degrees Cent.) slower than 19 inches per minute, permanent deformation took place at a rate slow enough for an amount of work-strengthening to be produced which was sufficient to cause other parts of the specimen to elongate also. But when a higher rate of deformation was employed there was not time enough for sufficient work-strengthening to take place, resulting in premature fracture.

The rate of deformation (plastic) necessary to produce an increase in strength without premature fracture occurring appears to vary according to the heat treatment and other conditions existing in the steel. This is shown by the fact that the specimens heated above the Ac_3 point of the steel could be pulled by the same slow and fast rates of deformation without premature fracture taking place in any of the specimens.

The rate of deformation necessary for sufficient work-strengthening to take place without premature fracture occurring seems to decrease as the extension increases. This is shown by the fact that the specimens annealed at 1400 degrees Fahr. (760 degrees Cent.) when pulled first with a slow rate of deformation followed by a faster rate elongated without fracturing prematurely.

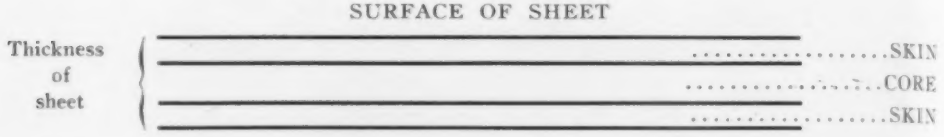
It would seem, then, that low carbon steel is best suited for deep drawing purposes when it is in the semi-plastic condition, since it can be deformed at a faster rate without premature fracture taking place, and since no stretcher strains form when the steel in this condition is deformed.

DISCUSSION

Written Discussion: By Felix F. Aloi, Seneca Iron and Steel Co., Buffalo, N. Y.

I would like to ask the authors of this interesting paper if the ferrite grain size of the group annealed at 1400 degrees Fahr. was considerably larger than that of the group normalized at 1750 degrees Fahr., also whether the carbon was in the form of pearlite and what was the Rockwell hardness of each group?

Stretcher strains are such an important factor in sheets that I would like to have the authors' comment on the following thought in regard to the formation of stretcher strains in sheet steel. Most of the steel sheets used today are made of "rimmed" steel; the ingot of this class of steel consists of a skin and a core. The relation of skin to core in sheets rolled from this type of ingot is shown in the following sketch.



For various reasons the skin is usually softer than the core and, therefore, has a lower yield point. When a sheet of this nature is stretched, the yield point of the skin is passed before the core has reached its yield point, therefore, plastic deformation must take place first in the skin. Does this difference in yield point have a bearing on the formation of stretcher strains?

Written Discussion: By Thomas Dockray, metallurgist, Eastern Rolling Mill Co., Baltimore.

A very instructive point has been brought out by Messrs. Winlock and Lavergne as a result of their very interesting experiments. Their conclusion is that a sheet or strip will perform better when in a semi-plastic condition.

There are two schools among consumers of these products—one puts the steel in this semi-plastic condition just previous to the stamping operation, while the other expects the mills to avoid stretcher strain formation and to do so the mill must cold work the material before shipment.

As shown by the authors, a final cold-rolled sheet, when the cold work has not been excessive, puts the material in the best condition for drawing. However, when cold work is performed aging to a greater or less extent will in most cases begin to take place in a short time and increase as time goes on. Thus in the case where this cold rolling is performed the mill has put the material in the best condition and the consumer should take advantage of this fact. In many cases where there is a continuous supply of material a shipment is only partially used and the remainder put aside and only used when it is most convenient, other subsequent shipments being used before this. Because of age-hardening the percentage of breakage is increased and the mill has to foot the bill. This is an unfair situation where the mill is penalized for saving the consumer an operation, namely, of putting the material into the ideal state himself just previous to the stamping.

These experiments bear out a phenomenon which I have been unable to

account for up to the present. In studying the effect of cold rolling sheets, a sheet would be split longitudinally, one-half tested in the annealed last condition and the other cold-rolled last.

With a certain degree of cold work this material would always test as good as, and sometimes slightly better than, the annealed last material. It was difficult to find some explanation of this phenomenon but the authors' experiments can explain it.

Mr. Winlock has a penchant for the study of plastic flow and he has brought out some very interesting facts. I wonder if he can offer some explanation of the following features.

In making a tensile test it is performed slowly until all plastic deformation has occurred and then pulled rapidly. When fracture takes place the strain markings have apparently pulled out, but if the surface be then polished with emery paper a pattern similar to the original strain markings is found. However, if a normalized only and a normalized and box-annealed sheet is compared, the markings on the normalized only sheet seem to be more predominant in height. These elevated areas seem to be a result of work-hardening in the original strained areas but the question arises as to why they should be more predominant in the stiffer sheet.

Oral Discussion

DR. ALBERT SAUVEUR:[1] This paper by Mr. Winlock and Mr. Lavergne deals with an important subject and is very instructive and suggestive. It is logical to assume the tensile test bar to be made up of groups of grains differing slightly in physical properties, at least in strength and ductility. Absolute chemical and physical homogeneity throughout the bar is not to be expected. On subjecting the bar to tensile stress, the elastic limit of a certain group of grains will be reached first and deformation will start at that point. This implies reduction of cross section and, were it not for the strengthening effect of cold work deformation, rupture would take place where elongation first started without permitting adjoining metal to stretch. There would be very little, if any, elongation of the bar as a whole. Deep drawing would be impossible or indeed any kind of drawing or stamping.

As matters stand, however, adjoining groups of grains elongate, being in turn strengthened by work and causing other adjoining unstrained groups to deform, etc. Might it not be then that the lines of Lüder represent slip bands of adjoining grain groups; that is, macro slip bands similar to the micro slip bands observable in individual grains. Note that both bands or lines are due to differences in level and disappear on polishing.

I find it difficult, however, to reconcile this otherwise plausible theory with some observed facts. For instance, as I understand it, stretcher strains do not occur in deep drawing, if the sheet is drawn shortly after its manufacture, assuming, of course, that it has received the proper amount of cold rolling. Aging causes the appearance of stretcher strains. It has been said that it is because aging restores the yield point destroyed by cold rolling. But how does this tie up with our theory of grain group slipping?

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[1]Gordon McKay Professor of Metallurgy, Harvard University, Cambridge, Mass.

It is readily seen that rapid testing by denying the necessary time for work-hardening and hence for the elongation of adjoining metal would result in premature fracture and little elongation, but why should a steel annealed above the A_3 point never suffer from premature fracture, regardless of testing speed? It differs only from the steel annealed at 1400 degrees Fahr. (760 degrees Cent.) by the size of the grain, which I presume to be larger.

Authors' Closure

We should like to thank Professor Sauveur for his helpful and constructive discussion. As we see it, stretcher strains represent degrees of difference in level between those portions of the metal which have slipped and those which have not slipped. When the differences in the level are large they are called stretcher strains and when the differences are very small, stretcher strains, although present, are not referred to as stretcher strains. For example, in deforming by tension the nonferrous metals, aluminum and copper, we get differential slippage (manifested by a roughening of portions of the surface) but no deep depressions. It would seem, then, that the occurrence of stretcher strains is dependent upon at least two things: (1) "work-strengthening" which we define as the *increase in strength per unit deformation per unit time* (and which is probably different for the different metals and may even vary in the same metal as plastic deformation proceeds) and (2) the fact that steel in the annealed or "aged" condition has a greater degree of elasticity and a more well-defined yield point than that of aluminum or copper or steel in the semi-plastic state. We are unable at the present time to describe the relative effects of these two observations.

We believe that one of the differences between the two lots of steel used in these experiments which may have an important bearing on the results and yet is not discernible by microscopical examination is the preferred orientation induced by the large amount of reduction by cold rolling and which is not removed except by heating through the Ac_3 point.

Mr. Aloi's comments are of interest. We did not make photomicrographs of the specimens, but microscopical examination showed that the specimens annealed at 1750 degrees Fahr. (950 degrees Cent.) had a somewhat larger grain size than those annealed at the lower temperature. The cementite was present in the spheroidized condition in the latter and in the partially spheroidized condition in the former. The Rockwell hardness of the specimens annealed above the Ac_3 point was 32 and of the other group 38.

We believe that anything which contributes to chemical or physical heterogeneity will increase the tendency to produce stretcher strains. But the heterogeneity such as that produced by "rimmed" steel is not the only cause because (1) stretcher strains occur in "killed" steel, (2) rimmed steel in the semi-plastic condition does not show stretcher strains after drawing and (3) if the low carbon surfaces are carefully removed, stretcher strains may still be produced.

The phenomenon which Mr. Dockray mentions is probably due to differences in the work-strengthening characteristics of the two steels about which little is yet known.

COMPARISON OF SHEET AND STRIP STEELS FOR DIFFICULT STAMPINGS

By Edward S. Lawrence

Abstract

This paper emphasizes the general differences in the manufacture of sheet and strip steels of the low carbon variety as utilized primarily for deep and extra deep drawing automobile stampings. Some of the most common defects and limitations encountered in the manufacture of strip steel for this particular and ultimate use are contrasted with some of the more common defects attributed to the manufacture of sheet steel. The adaptability of strip steel as made on a continuous four-high mill as breakdowns to be used on a conventional two-high sheet mill is emphasized.

The influence of deep drawing strip steel on the market formerly held by sheet manufacturers is discussed. The rapidly improved methods of sheet rolling are defended.

The various physical standards as are now demanded by the consumer of sheet and strip steels are criticized. Emphasis is laid to better cooperation between manufacturer and consumer as regards their research and development, the author indicating that close co-operation will be extremely beneficial to both.

THIS paper is limited to the comparative study of low carbon strip and sheet steels produced in wide, thin gages as utilized for difficult stampings, principally those stampings used for and in the manufacture of automobile bodies.

The physical, processing, and economic comparison of sheet and strip will be briefly discussed and the advantages and disadvantages of each and to one another will be correlated with the idea of ascertaining, if possible, the best deep drawing sheet of tomorrow, which, undoubtedly, will come from a combination of our present strip and sheet processes (1).[1]

In spite of the fact that the continuous rolling of wide strip has

[1]The figures in parentheses refer to the bibliography appended to this paper.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author is a member of the society, and is metallurgical engineer for the Duraloy Co., Pittsburgh. Manuscript received June 16, 1931.

received marked attention and comment since its entry into the automobile body field some four years ago, we are somewhat concerned with the advantages and defense of the conventional two-high sheet mill whose modernization and marked improvement of product, we believe, has been momentarily overlooked.

This paper is further presented with the thought that the author does not believe that any broad, comparative treatise on sheets and strips for deep drawing purposes has been brought to the attention of the consumer. By this we mean that while the subjects of sheet and strip have been discussed separately and quite in detail (2), they have not been discussed collectively. A careful review of the literature on the above subject matter as issued during the past five years indicates that not only are the papers and discussions somewhat contradictory, but, in many cases, are and have been made, ambiguous and misleading. This is because of the fact that late information pertaining to these industries has been intentionally withheld by the suppliers. While this is regrettable, yet it is quite natural and expected.

Nor is the consumer of sheet and strip steels exempt from some criticism. The revolutionary changes made in almost lightning rapidity within the sheet and strip industries practically parallel the rapid changes which have occurred within the automotive industry itself. Automobile body designs and their attendant and ever-increasing deep and more complex stampings, are constantly being changed. It, therefore, has become almost necessary that, considering the shape of the stampings, various complications of drawing, and the surface finishes as demanded, the suppliers of sheet and strip set up practically separate treatments for each and every standardized automobile body part. Therefore, coupled with the constant changing of these parts, it has, with undue hardship, prevented the efforts of suppliers to really standardize various thermal and mechanical treatments of their strip and sheet. For this condition the user of sheet and strip is largely responsible. Furthermore, the consumer might, and in the future probably will, contribute considerable valuable information to his suppliers, but so far as generally reviewing this matter openly with them is concerned, he has thus far failed to contribute anything of marked consequence to the advantage of sheet and strip mills, and, of course, indirectly to himself. It is a known fact that these data are available and would be of great material assistance to the suppliers even to the extent of not only improving the drawability, but also reducing the high ultimate price, if only this co-operation could be

realized in the light that its divulgence would materially aid all concerned.

Tonnage Comparisons of Sheet and Strip

It seems quite appropriate, at the beginning, to correlate the tonnages of both sheet and strip steels utilized by the automotive industries since we are all familiar with the fact that since the period of 1926-1927 the mass production of automobiles has necessitated a marked increase in the output of both products.

In early 1927 the loose rolling sheet mills found themselves faced with the problem of trying to meet the demand for the great tonnages of deep drawing sheets then being purchased by the automotive industry. We are all familiar with the fact that this great demand for sheets at that time was the result of mass production of automobiles. The sheet industry, in order to cope with the situation, was putting considerably more hot mills into operation, which, of course, necessitated increased equipment for pickling, annealing, and cold rolling. This was the psychological moment for manufacturers of strip steel to jump into the ring and proclaim themselves the answer to the production of large tonnages of wide, and thin gage deep drawing sheets.

Up to this time, the continuous rolling of strip steel in narrow widths (up to 24 inches) was fairly well established and well worked out in detail. To be sure, some experimental work had been done on wide thin strip rolling, primarily in view of working this product into the field now predominated by the sheet industry. Much credit must be, and is, given to the farsightedness and incentiveness on the part of strip producers, as well as several sheet mills, who were willing to gamble their knowledge of processing thin narrow strip against the great rewards to be found in successful continuous processing of strip in even greater widths than 24 inches. It is sufficient to say that since 1927 strip manufacturers have gradually cut down and into the market formerly held quite securely by the sheet industry, which may or may not be the answer.

For concrete examples, in 1927 the automobile industry bought 1,103,950 tons of sheets from the sheet industry itself and only 477,437 tons from the strip industry. In 1928 the strip people practically doubled their output into the automotive field which shows the reaction that the automobile industry had toward the use of strip steel, even in those days of early development. It is not our intention in this paper to gain our point by dragging out this discussion

through the medium of long columns of statistical figures, but we do feel that this comparison will show the inroads made by strip into the sheet industry.

The year 1929 was an excellent year for everybody, including even the automotive industries. In that year, they bought 1,608,807 tons from the sheet industry, which represented approximately 37 per cent of all sheet output. They also bought 1,180,663 tons of strip, which represents approximately 61 per cent of the strip output. Thus, it can be seen from this last figure that most certainly the strip industry should feel pleased with their venture into this automobile body market in view of the fact that more than half of their output was, for the most part, absorbed in the form of auto body stampings. Another fact of interest is that ever since 1927 the strip industry has gradually cut down the difference between its automotive tonnage and the predominating tonnage of sheets as also supplied to the automobile industry. The difference was 726,513 tons in 1927, 448,178 tons in 1928, and 428,144 tons in 1929, while the year 1930 shows that the difference is down to 398,952 tons.

The year 1930 was a disappointment to the automobile industry and its allied industries to the extent that it purchased only 1,125,902 tons of sheets, which represented approximately 36 per cent of sheet output, and, furthermore, purchased only 726,950 tons of strip, which represented approximately 55 per cent of the output of that industry, a decrease of 1 per cent for sheet and 6 per cent for strip over the preceding year. These figures are not bad when one considers that during 1930 only 3,300,000 automobiles and trucks were sold which was a decline of practically 40 per cent over the output of 1929. Along with this, we must remember that new and improved sheet mills were built in 1930, and at the same time, marked improvements in wide strip tonnages in all respects were quite noticeable. Thus, 1930 showed that so far as supplying thin, deep drawing material to the automobile industry was concerned, the sheet industry held a slight edge over the strip industry, even though both lost about 40 per cent of their usual automobile trade.

We have introduced these figures merely to show the relative, and somewhat marked, strength up to the present time, of the strip industry and its influence on the automobile markets which it was striving so hard to serve. The rapid addition of continuous rolling mill equipment by the outstanding steel companies of this country indicates its future and possibly may attribute to its success, and per-

haps its downfall. An enormous initial investment, including a slow capital turnover, means that if strip is to be produced at low costs, it must naturally turn out large tonnages. This is possibly the longest and strongest argument now in favor of the conventional sheet mill.

Some Advantages and Disadvantages of Strip

It must be remembered that unless a continuous mill is kept running close to capacity, it will hardly be expected to make much, if any, profit. With these facts in mind, we are now confronted with the fact that approximately 75 per cent of the present sheet-making capacity of the United States is in the hands of companies who are utilizing, or are about to utilize, the continuous methods of producing strip sheet in wide thin gages, all processing of which is claimed to be under a very broad and comprehensive patent structure. The ever increasing output of continuous hot and cold strip mills indicates that more tonnages of sheet material will be produced than can probably be absorbed for some time, at least, and unless this tonnage is curtailed, we are led to believe that we will see greater comparative price cutting in the field than has been heretofore realized or anticipated.

The influence of low-priced strip for deep drawing stampings has been made manifest in the prices of sheets whereas from January 1927 the base price of 20-gage sheets at Pittsburgh has dropped from 4.20 to 3.10 cents per pound. In addition to this, the extras for deep drawing grades and finishes were somewhat relinquished in 1929 by combining and averaging the extras for deep and extra deep drawing grades, all of which reductions do not show up in the base price. Therefore, marked concessions have taken place in automobile body sheet prices through the influence of strip, and have necessitated, in turn, improvements in conventional sheet rolling, which will be later discussed.

We beg your indulgence for a moment to read a portion of an article on the continuous rolling of sheet steel published in May 1927 (3) when strip was first beginning its drive on the automobile industry. This article is worthy of reviewing as it indicates that the economic background for continuous rolling is an important one, and further reveals that under present conditions, the earlier thoughts on this subject should still be respected. Furthermore, it indicates that of what little knowledge was available at that time little has been divulged since then. In spite of certain enthusiasms as regards this

new venture of strip, it has indicated its enthusiasms with reservations.

We, therefore, quote from this article as follows:

> "As regards the present economic background of the sheet business, certain features are in favor of and certain against the continuous sheet mill, with the balance probably on the favorable side. The demand for sheets has been steadily increasing, and such moves on the part of the industry as the formation of the American Sheet Trade Extension Committee, are certainly helpful in this direction. The advancement in knowledge of sheet stamping, pressing, etc. is also increasing the range of users of sheet. The new varnishes and lacquers which make sheet steel articles more durable are expected to be a contributing factor in the same direction, and yet with the demand for sheet steel decidedly on the increase, the profits of mill operators have been low and show no tendency upward. This is ascribed by every one concerned to the intense competition for business among the operators and the very keen ability on the part of the buyers, particularly the larger companies, in turning this competitive condition to their benefit. The state of the industry being thus, there is every reason to believe that the lower prices which the continuous sheet mills are already quoting and at which they can make better profits (assuming that everything works out all right) than the noncontinuous mills at their higher prices, will attract the business their way. The tendency toward the so-called hand-to-mouth buying is cited as against the interests of the continuous sheet mills in that it is apt to break up business into parcels which may eventually prove too small for them to handle. So far, however, there does not seem to be any indication of this as seriously affecting the business of the only existing mill of that kind, and there is every reason to believe that with the price attraction, purchasers will be willing to give sufficiently large orders to get the full benefit of the lower quotations. The continuous sheet mills will roll every width between strip and approximately 42 in. and every gage, and are therefore capable of taking care of any market requirements. There is very little doubt, therefore, as to the permanency of this new development. In the United States continuous sheet rolling has come to stay. There is every indication that it will remain essentially an American development. Considering the profound changes which it has created in a great industry and the further fact that no new inventions are really involved in it, it is rather surprising that no continuous sheet mills have been built before. They have, however, come to stay."

The author of the above quoted paper certainly made a good statement when he said that "assuming that everything works out all right," the continuous sheet mills will outsell the conventional sheet mill product. Naturally, at the present moment, with these two industries in the midst of an economic battle for mere existence, let alone profit, the statements from this quoted article are well ex-

pressed and proved to be true at the present time, as "the tendency toward the so-called hand-to-mouth buying is cited as against the interest of continuous sheet mills in that it is apt to break up business into parcels which may eventually prove too small for them to handle."

The present buying for immediate consumption presents orders which can hardly be handled on these large continuous mills, any one of which can hot roll in a day tonnages which the average sheet mill would be glad to get out in a week. Therefore, these small orders demanding almost immediate delivery for ready consumption are in such odd gages and sizes that it presents great difficulty for strip manufacturers to produce this material and still make any profit.

On the other hand, the sheet people by their noncontinuous mills and through the medium of their modern and revamped equipment which has helped speed up their processing, are able at this particular time to quite readily fill such small and nondescript orders. While it is a well-established fact that their profit is very slim, nevertheless their maintenance and operating costs are flexibly adjusted to the product which they make, and, therefore, their chances for making money on such orders are possibly slightly better than for those producing strip steel. The continuous hot and cold rolling strip equipment maintained for high tonnage production is quite analogous to the latest type of continuous heating or normalizing furnaces in that the upkeep and operating costs continue whether the mills or the furnaces are running 50 or 100 per cent capacity. Thus, in a continuous heat treating furnace, the fuel costs remain approximately and practically the same so long as a certain temperature must be maintained and the interest on the investment will not vary with the tonnage output. Likewise, the electric power for driving the continuous mills or furnaces is not appreciably reduced by small production; in fact, the whole theory of high tonnage equipment is that the highest tonnage involves the lowest cost. Thus, when the automobile industry wants a few sheets instead of a few tons of an odd gage and size, the costs of producing such an order on this continuous equipment jump to a point where hardly sufficient profit is made to pay the interest on the investment.

It is quite possible that within a few years continuous rolling mills will be further perfected to the point that continuous wide strip (36 to 48 inches) can be continuously hot-rolled, in one heating, down to gages which fall within the average acceptable range of the auto-

mobile industry, namely 18 to 22 gage. Until then, the hot rolling of 36 to 48-inch strip will more or less commercially stop at around or about 16 gage. The 16-gage strip will then be continuously pickled and recoiled, and then be reduced to the desired gage by continuous cold rolling on four high and cluster cold mills, which is the present practice(4).

Some thought has been given to continuous pack rolling of hot strip producing as low as 24-gage with the possibilities of getting still lower (5). However, from all information available, this has been attempted but is not as yet a commercial success, although we have no doubt but that the near future will reward the persistency and incentiveness of those working on this phase of the mechanical treatment of strip.

Thus, we have hot-rolled strip in widths up to 48 inches which are reduced to the desired gage by continuous cold rolling. This continuous cold rolling through cross-sectional reductions up to about 90 per cent has a decided advantage for strip over sheet as used for deep drawing purposes, particularly from the standpoint of surface after draw. Cold work on a sheet rolled on a two-high mill will often cause grain growth on or near the surface of the sheet through subsequent annealing, a condition which remains and can only be obliterated by a normalizing heat treatment. This surface grain growth might allow the body part to be satisfactorily drawn to shape, but the finished part would show a granular surface due to this abnormal surface growth due to critical straining through cold working. This condition is not likely to occur in strip steel because this cold rolling reduction is so great that large grain growth does not occur in the usual temperature ranges of subsequent annealing. This is explained in that the subsequent annealing temperatures of strip do not occur within the range of critical grain growth, which range is dependent on the amount of strain by cold working induced in the material(6).

Strip steel, on the other hand, commercially presents a much harder, stiffer, and smoother surfaced material than is produced by sheet suppliers for the same purpose. While that comparative phase will be discussed later, it is well to note at this point that strip steels, by reason of their heavy cold roll reductions in particular, present a sheet for drawing purposes whose elastic limit is on an average higher than that of sheet, and with many difficult body stampings, this feature is a decided advantage (7). The author knows of a number of cases where extremely difficult body stampings were produced with

less breakage from a normalized strip steel where the elastic limit was approximately 70 per cent of the ultimate strength, whereas conventional sheet steel of the same carbon content showed greater breakage, even though it was normalized and box annealed and even had the same chemical analysis. The apparent and marked difference indicated that the sheet steel had an elastic limit of only 60 to 65 per cent of its ultimate strength, whereas the elastic limit of the strip was approximately 10 per cent higher.

While on the question of hardness and stiffness of cold-rolled strip steel, we might mention that this product shows a tendency to grow hard or "age." This aging effect, while of a minor magnitude, still causes strip producers no small amount of worry and is analogous to stretcher strains which have always seemed to bother the sheet producers. This aging of strip steel indicates a gradual increase in hardness following its final cold working for a period of several weeks (8). This aging is manifested in that on an 18-gage strip, for example, the Rockwell B scale hardness jumps from 3 to 6 points and the Olsen ductility drops from 5 to 20 points within the above mentioned time. This aging effect is sometimes sufficient to cause a marked increase in the breakage of the automobile part for which it is intended. However, this particular problem is being thoroughly investigated and undoubtedly it will be overcome (9).

In conclusion, so far as the strip mill is concerned, we believe its importance from the standpoint of tonnage has been over-estimated, but there are many distinct advantages to strip, such as accuracy to gage, and surface finish, which is not possible at present in conventional sheet manufacture. However, the continuous hot rolling in single thickness in a single heating leaves strip at about 16 gage in the wide widths in which we are interested. We, therefore, agree with the thoughts expressed by Shannon, Jones, Melaney, and others in that hot-rolled strip can be cut into breakdown sizes and finished to the lighter gages on the conventional two-high sheet mill to the advantage of existing sheet mill equipment and resulting in a larger output for strip tonnages. Without going into this subject any further, we refer to Shannon's recent and excellent contribution (9A) for details which are worthy of recording, but which time does not permit. We do, however, wish to leave the discussion of strip by quoting Bennett (10) as follows:

> "Giving due credit to the importance of recent developments in the rolling of wide strip or sheets, which mark distinct economic and human-

itarian advances in steel mill operation, the new mills have certain inherent limitations, which should not be overlooked in a study of their relations to old style mills. In some cases, a group of hand mills may well complement a continuous mill installation to secure a desired increase in plant capacity. For the gages at present within the range of the new type mill, it will be found that cost of installation of such a mill is practically that of the equivalent tonnage group of old style mills, without, however, the flexibility of operation of the single mills. Until the new type mill is developed to the stage of satisfactorily and economically handling practically the entire range of sheet mill gages and widths, the old style mills have their field and may well supplement the new type for some time to come."

The Conventional Sheet Mill

There are in this country over 800 conventional two-high hot sheet mills, about 50 per cent of which are devoted to the production of high grade sheet steel such as might be used by the automotive industry. As we have already stated, back in 1927 the advent of the wide thin strip caused considerable worry and unpleasant predictions to the sheet mill owner, who probably felt that his conventional mills were about to be scrapped. This equipment represents an investment of approximately $200,000,000. The sheet industry was, at that time, producing about all the tonnage that they could possibly roll as the automobile industry was demanding deep drawing sheets faster than it could be run out in these mills.

The principle of hot rolling by hand on two-high nonreversing mills has been, for the most part, practically unchanged since rolling methods of this nature were utilized 200 years ago. It is only within the last fifteen years that the loose rolling of packs into sheets utilized for deep drawing stampings has come to the front, and the advances made in the methods of processing such sheets have been almost as great in these last fifteen years as during the total existence of this particular art. Therefore, when the strip industry made a bid for the increasing tonnages of full-finished deep drawing sheets required for automobile bodies, the sheet industry itself was again forced to take account of stock and once more seek to defend itself by further improving its equipment.

These improvements have been marked and diversified. The crude pack and pair heating furnaces have given way, in a majority of mills, to continuous furnaces which practically tripled the output of packs and pairs, thus enabling greater and more uniform production of good sheet, from the standpoint of the hot mills. Men were

cautioned and carefully trained in the art of producing loose rolled sheets so that less variation in gage thickness from edge to center was encountered, more attention was being paid to the condition of the hot mill rolls both from the standpoint of their shape, and cleanliness of surface. Improvements in pickling and two-high cold rolling were also carefully investigated and corrected. The sheet industry was first to recognize and utilize extensively continuous normalizing furnaces (11). These continuous normalizing furnaces not only cut down the time of processing and eliminated the first box annealing of steel, but they produced a more uniform, deeper drawing and tougher sheet through this recrystallizing heat treatment. Now practically 90 per cent of all automobile body parts demand a normalized basic structure. Most certainly credit is due to the sheet producers who first installed these somewhat expensive continuous sheet normalizers, thus introducing on a commercial basis a sheet of superior drawing qualities and finish than ever was produced commercially by the now somewhat antiquated double box annealing methods. It is well to note that the strip manufacturers have been forced, to a marked extent, to normalize their strip steel where extremely difficult drawing operations are necessary. We mention this fact because the strip supplier felt in the beginning that he could finish his strip on the hot mills at such a high temperature that by coiling the hot strip, he could bring about a normalized treatment in the coil itself, or he could box-anneal his severely cold-rolled strip and produce a similar grain to that obtained by normalizing. These procedures, however, have never proved a commercial marked success where extremely uniform grain structure is deemed necessary, and the body part presents an extremely deep draw.

At this point, we would like to state that this paper will not be interspersed with photomicrographs showing low carbon steel and strip having normalized or single and double box annealed grain structures. Those who have read this paper or are here today are fully aware of the fine, thoroughly equiaxed grains resulting from correct continuous normalizing treatment, and the larger, somewhat irregular, grains as from box annealing. The author feels that those who have preceded him in the discussions of sheet and strip have not only satisfactorily covered this phase, but it seems quite unnecessary to take the time to explain these differences of grain size and treatment by a lengthy, and somewhat elementary, treatise on metallography.

Therefore, to proceed with the discussion of conventional sheet making, we find that the sheet manufacturer has not only improved his equipment for thermally and mechanically processing his sheets, but he has also taken steps to handle this high grade product by installing certain conveying equipment which is quite necessary for the maintenance of a good surface on such sheets. As we have already stated, the economic situation today places the sheet manufacturer in an excellent position to quickly obtain the most odd gage and size orders for sheets as he can utilize his noncontinuous and, therefore, quite flexible, equipment to much better advantage than the continuous strip manufacturer could ever possibly hope to do.

There are at present, in the author's estimation, two steps of manufacture which could be decidedly improved upon by the manufacturers of sheet for difficult stampings. One of these improvements is traceable to the fact that the majority of surface defects encountered at inspection are traceable to defects caused on the hot mills, or when the sheet is rolled from sheet bar to breakdown and then into finished hot-rolled sheets. These defects are not necessary to be repeated here because the majority of those sufficiently interested to read this paper are fully acquainted with the majority of such hot mill defects, and even their cause and remedy. The author believes that by utilizing breakdowns as derived from hot-rolled strip steel instead of the usual sheet bar, that these strip breakdowns in pack form would eliminate a great many defects heretofore encountered and acknowledged as difficult to overcome when breakdowns rolled from sheet bar on sheet roughing mills are utilized.

By thus utilizing strip breakdowns, a flexible noncontinuous sheet mill can practically double its output on the hot mill floor by changing all roughing mills to finish-mills, and all continuous or noncontinuous pair heating furnaces to continuous pack heating furnaces. Naturally, of course, this increased output will demand larger and greater facilities for pickling, cold rolling, normalizing, and box annealing, but it is not necessary to discuss this phase at this point.

The other improvement which could be made in sheet production is through the medium of better thermal treatment. It is acknowledged that through the medium of a correctly constructed normalizer, the sheets are heated and cooled so uniformly that if the steel is clean, the resultant normalized structure is uniform and equiaxed throughout the entire sheet. If this basic normalized structure is correct, we assume that for a full-finished sheet it is usually followed by pickling,

cold rolling for surface, and then box annealing for a softening action (because normalizing and cold rolling together present a somewhat stiff and hard sheet, although very ductile). This box annealing usually calls for a heat treatment at low temperature of a large mass of steel which is rarely, if ever, uniformly heated throughout.

This heat treatment of a large compact mass of sheets presents variable physical properties which have a marked effect when the sheet is drawn to the shape desired. While nobody has as yet publicly presented any sort of a solution to this problem, it is believed that time is not far distant when full-finished normalized sheets will be continuously heat treated in possibly a bright annealing furnace at a low temperature, which will then allow the sheet manufacturers to present a uniformly heat treated product having uniform physical properties throughout the entire shipment. The utilization of breakdowns from strip mills in a modern hot sheet mill, such as proposed by Wean (12), and already reduced to practice in one of the country's most modern of sheet mills (13), we believe will allow the existing sheet mills to seriously combat the advances being made by the strip manufacturers in their particular field.

It is indeed true that both sheet and strip steels utilized for difficult stampings have many treatments in common, but the main difference between these two parts, at the present time, is in their method of production. The strip mill may eventually continuously hot roll wide strip into the desired gages and widths, and when this occurs, they will again threaten the sheet industry as it has never been threatened before. In the meantime, however, the sheet industry has stepped up not only its production through the use of improved mechanical and thermal equipment, but it has assumed semi-continuous methods of handling which are somewhat flexible, and it is not unlikely that they will continue to hold their own for some little time to come.

Relation of Consumers to Sheet Suppliers

As to the relative advantages and disadvantages of sheet and strip, as just briefly discussed, we cannot overlook the fact that recent mergers for the sake of economy have helped to concentrate and simplify for the consumer the sources from which he can obtain his deep drawing materials (14). This marked concentration of activities has helped the producer to combine his technical developments and research so that, at the present time, he is in an excellent position

to serve well his customers with various grades of deep drawing sheets for practically every use.

The consumer is, therefore, much better off than heretofore, as the research and study given to sheet and strip enables him in turn to study the results of such research and to purchase his materials under somewhat standardized grade names and numbers. We find that the supplier of sheet and strip has, in spite of activities to keep up with production, found time to publish some of the results of investigations of deep drawing materials. We refer to such data as published by some of the leading manufacturers, who, through the medium of their publications, have attempted to simplify the purchasing of high grade deep drawing sheets and strips. Such publications as mentioned are typical examples, and should be acknowledged and appreciated by the consumers of sheet and strip (15).

On the other hand, we find very little data published on investigations conducted by the consumer. However, the papers and articles by Graves, Brown, Winlock and Kelley, and Morton are worthy of reference (16). But through the pens of these men have come the majority of contributions on this subject of sheet and strip from the consumer's standpoint. The author, therefore, urges, through the medium of this article, that more consideration be given by the consumer to the wishes expressed by the manufacturer relative to simplified means of specifying orders. It is indeed unfortunate that the manufacturer has been forced to accept not only physical or chemical limitations, but also specific limits on breakage, simply because the tonnage usually warranted the acceptance of the orders on the chance that they would perform as per the demands of the consumer. If the physical properties are demanded along with a minimum breakage, the consumer should not hold the manufacturer responsible for a certain range of chemical analysis, or, if the analysis is specified, the manufacturer should not be held for the physical properties obtained, although this latter combination is much easier to carry out and hold to in the process of manufacture.

We find the consumer attempting to run a certain gage and size of both sheet and strip for the same deep drawing part and, in this respect, a great deal of trouble is often encountered. To be more specific, we refer to a recent paper by Winlock and Kelley (17). These men have contributed as much, if not more, to a better understanding and co-operation between sheet and strip manufacturers and the producers of automobile bodies than any other authors up

to the present time. They have given the manufacture of steel intense study, which should have its effect on even the steel producers themselves in that their deductions and conclusions can well be adapted to mill processing. For example, these authors, in discussing sheet and strip, emphasize the fact that a die properly set up for a soft sheet will not produce to good advantage the same stamping as made either of a somewhat stiffer or harder sheet or strip. This statement is, we believe, quite true.

The clearance between punch and die is often set up for sheet steel which, on an average, will show a difference of about 2000 to 10,000 pounds less tensile strength, and approximately the same less number of pounds difference in elastic limit over a normalized sheet or strip steel. This difference in tensile strength and elastic limit might be taken into consideration when we know that we can produce for these dies, sheet or strip showing this marked difference in ultimate and elastic strengths although the Rockwell hardness and the carbon content of both may be identical. This stiffer or harder sheet or strip then produces wrinkling in the part to be formed. For this reason, we cannot agree with Graves (18) who states that "The Rockwell test is an indication of tensile strength."

It might be well to reminisce for a moment on the dies used on the various grades of deep drawing sheets which have been utilized in the past few years in order to more fully illustrate wherein the consumer has perhaps somewhat failed to keep up with the change in materials which he is attempting to draw to shape. Prior to the advent of sheet normalizing furnaces, double box-annealed sheet was used, which was soft, very ductile, and had a fairly large grain structure. This soft, putty-like sheet formed shallow stampings quite readily when sufficient clearance was allowed in the dies. More difficult and deeper stampings demanded a normalized and box-annealed sheet, which, having a much finer but tougher grain structure, also induced a certain amount of stiffness not heretofore encountered. This resulted in a buckling of the material in the dies having a large clearance, and, therefore, in order to use this stiffer sheet, dies were altered to take care of this change in processing. Now we have strip steel, which, although normalized and possibly box-annealed, has a much smoother surface and a greater tendency towards stiffness in forming than the normalized sheet steel, even though, as we have said before, both may have the same Rockwell hardness and may even show the same ductility value.

It must be expected that consumers will have to take care of this discrepancy and, therefore, we are led to conclude that they must either specify strip or sheet for the particular part intended, or make allowances in the adjustment of their dies for these two mechanically different processed products. Furthermore, the thickness of material desired for the automobile body part should be specified in decimal thickness. If ordered in gage thickness, sheet and strip will vary, as sheet is rolled to United States gage and strip is rolled to Birmingham wire gage. The decimal difference between these two products for the same gage number, coupled with the allowable gage variations, will quite often cause breakage of the part even though the sheet or strip is quite capable of making the draw.

Importance of Microstructures

If the sheet and strip manufacturers are fully aware of the shape and depth of draw necessary for a certain automobile body part, they are able to produce the specified physical characteristics usually demanded by the consumer. However, in so doing, they usually rely on taking quick physical tests, such as Rockwell hardness and either Olsen or Erichsen ductility tests, as a means of record. However, if they are alert to the situation they will, along with these quick test records, examine and record grain structures. From that point on, the manufacturer must rely on the consumer to inform or let them observe the action of this steel under the presses, and from these observations, the mills can probably well duplicate the material.

The consumer, on the other hand, usually armed with only a very meager knowledge of sheet and strip processing, attempts to segregate good and bad shipments by hardness or ductility tests. In turn, the consumer specifies the various physical properties based on his observations of the test pieces taken from various parts of the shipments, which is often made up of several heats. Thus, Graves indicates (18) "the Rockwell test is an indication of tensile strength" and "have tentatively set a limit on hardness of B-43 and B-53 on normalized sheets and believe this to be the most desirable range."

We are of the belief that this is a rather wide range of hardness. Sheet and strip manufacturers know that they would have little difficulty in meeting this range of hardness limits, although it would be quite questionable as to whether the maximum and minimum of this range would work for the same part intended. A correct standardization of physical limits and even microstructures to be

placed on sheet and strip is a goal yet to be attained, but we predict that operation in the presses, together with a specified grain size of the metal, will eventually supersede the present general chemical and physical specifications. However, before we ever reach such a specification, we must rely first on the heartiest co-operation between producer and consumer, as well as a better understanding by the consumer as to how his materials are made, and by the manufacturer as to how his product will be used. As the matter now stands, the only reliable test for ductility is a study of the grain structure of the material and the actual operation of the material in the presses, and this should be the only specification. From the standpoint of resulting surface, the Erichsen or Olsen cup test proves a quick method of determining the appearance of the stamping as drawn to shape, particularly at sharp corners and bends. The hardness of a sheet or strip is merely an arbitrary and comparative number as there are any number of means of processing whereby certain hardness value can be obtained, but with no assurance that the material will work satisfactorily.

Conclusion

We, therefore, predict, in conclusion, that the present trend of deep drawing sheets and strips will be toward a limited number of continuous strip mills, which will furnish to the automotive industry not only wide and thin gage strip after its own processing, but, in turn, will operate close to capacity and at a profit by supplying continuously hot-rolled strip cut to length to form breakdowns for the conventional sheet mills. These strip mills will make profits only by the continuous rolling of large orders.

The sheet mills, on the other hand, by their flexibility are in an excellent position to handle the nondescript orders with profit. By using pickled hot strip breakdowns instead of sheet bar, they will eliminate roughing mills and their attendant pair heating furnaces, increase their output, and decrease somewhat their processing costs, and above all, by utilizing these breakdowns, eliminate a great majority of their surface defects which have been attributed to hot loose rolling practices. Furthermore, means for giving sheet and strip a continuous low temperature anneal will eventually come, thus eliminating irregular physical properties brought about by the present mass box anneal.

As long as the present distinctly different processing methods

exist between sheet and strip, we will always have a differential of stiffness and hardness between these two products. The consumer must make allowances for these differences, and while it means practically nothing so far as ductility, grain size, or depth of draw are concerned when comparing the two products, it does, however, influence the type of punch and die setup. It has already been indicated by Kelley and others (19) that the high stiffness as characteristic of strip steels, causes an excessive wear on the dies. As these and other factors are gradually brought forward to the attention of both the strip and sheet manufacturer, as well as the consumer, there will be a tendency towards fewer grades of deep and extra deep drawing materials. This, however, will come only when the sheet and the strip manufacturers are willing to divulge to their consuming public the basic knowledge of the manufacture and application of their sheet and strip steels, and furthermore, that the consumer, in turn, will study more carefully his equipment for pressing and drawing, and divulge such knowledge, in turn, to his suppliers.

It is to be regretted that even though the basic and chronological order of both thermal and mechanical treatments of sheet and strip are more or less universal among the sheet and strip mills of today, such information is secretly held in abeyance which, in turn, is retarding the study of the art of deep drawing materials. Certainly we do not anticipate that the manufacturers will divulge their exact procedures of manufacture, but we do believe that the revelation of their basic processing will be not only found to be identical with their competitors, but will give the industry a sounder basis on which to go forward.

Realizing that combined efforts will serve the automobile industry and its allies to distinct advantage, the author believes that if any such thought or action is derived from this particular paper, then its object has been accomplished.

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EFFECT OF NORMALIZING ON THE GRAIN STRUCTURE AND PHYSICAL PROPERTIES OF AUTOMOBILE SHEET STEEL

By William F. McGarrity and H. V. Anderson

Abstract

A brief description of the rolling and heat treatment of automobile sheets is given, and a resumé of the X-ray crystallographic method of examination of such sheets is described. Internal strains, grain size, grain orientation, and directional properties are clearly shown by this method of examination. Hot-rolled specimens of commercial automobile fender stock were treated at temperatures ranging from 1400 to 1800 degrees Fahr. X-ray diffraction patterns were taken at 100-degree intervals. Erichsen values gave a measure of the workability of the metal normalized from the various temperatures.

Increase in preheating time made no difference in the resulting structure, while increase in the soaking time gave a slightly larger grain size and slightly higher Erichsen values. A rate of cooling slower than strictly normalizing resulted in a considerable increase in workability results. A temperature of 1700-1750 degrees Fahr. gave the best X-ray structure, confirming photomicrographs and Erichsen tests. Directional properties were not completely removed after seven minutes soaking at 1800 degrees Fahr.

Introduction

THE automobile industry has increased to such a great extent during the past twenty years, and the automobile manufacturer's requirements for steel have become so exacting, that close control of the quality of the steel used must be maintained. The problem of producing steel sheets which will meet these precise demands as

This paper is based on a thesis submitted to the faculty of Lehigh University in partial fulfillment for the degree of Bachelor of Science in Chemical Engineering.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. Of the authors, William F. McGarrity is a member of the society, and is associated with the research department of The Youngstown Sheet and Tube Co., Youngstown, Ohio, H. V. Anderson is associate professor of chemistry at Lehigh University, Bethlehem, Pa. Manuscript received June 2, 1931.

to deep-drawing qualities, ultimate tensile strength, finish, etc., presents a real and wide field for constant improvement of process methods and examination of the finished product.

The object of this investigation was to study the effect of normalizing upon automobile sheet steel by means of X-rays, photomicrographs, and Erichsen tests.

The term "normalizing" is defined as "air cooling from a temperature exceeding the critical range." Its purpose is:

1. To eliminate the crystalline deformations due to the rolling.
2. To relieve internal strains.
3. To obtain equiaxed grains.
4. To obtain sorbite from the new fine-grained structure by the cooling, and thereby regulate the hardness and ductility of the material.

Steel which has been cooled in still air (such as normalized steel) possesses a slightly higher ultimate tensile strength and a ductility often better than a similar steel which has been annealed.

A typical continuous normalizing furnace for treating 20-gage material 30 inches wide and 72 inches long consists of a 100-foot heating zone followed by a 50-foot cooling zone. As pointed out by Lawrence[1], the speed at which the material can be conveyed through the furnace depends upon: 1—Hearth width and length of heating zone. 2—Carbon content of the material. 3—Elimination of internal strains. 4—Grain size desired. 5—Temperature available in heating zone. 6—Rate of preheating. 7—Time of cooling. 8—Thickness of metal being heated.

In the above furnace, the approximate speed is thirty linear feet per minute, so that the sheet would be subject to heating conditions for about three and one-half minutes. Of this, about two-thirds of the time is heating and one-third is soaking.

The temperature in the normalizing furnace is usually held at 1850-1950 degrees Fahr., the temperature of the sheet being 1700-1800 degrees Fahr., depending on its condition and the heat treatment desired. It requires a sheet temperature of approximately 1750 degrees Fahr. to eliminate strains due to the rolling, and to produce a new grain structure in the metal. Certain conditions such as nonmetallic inclusions, banded ferrite, etc., will ap-

[1]E. S. Lawrence, "Continuous Heat Treatment of Sheet Metal," *Heat Treating and Forging*, Sept. 1929.

parently cause the metal to respond with some difficulty to the theoretical critical temperature for recrystallization. For instance, a 0.07 per cent carbon steel should theoretically respond to treatment for internal strains, etc., when heated to 1650 degrees Fahr. In practice, however, a temperature approximately 100 degrees Fahr. higher must be used to accomplish this.

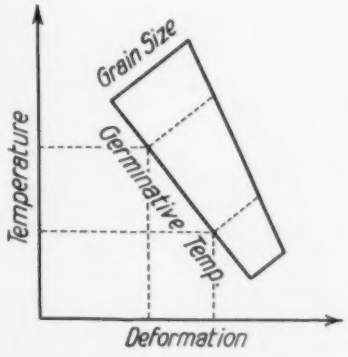


Fig. 1—Relation of Grain Size and Germinative Temperature to Deformation.

We were primarily interested in the deep drawing properties of the sheets, hence the specimens were subjected to a cupping (Erichsen) test, the Erichsen values giving a measure of their workability.

The workability of a sheet is directly dependent upon grain size and freedom from strain. When a hot-worked low carbon steel is allowed to cool undisturbed, the distorted ferrite grains will be spontaneously annealed until the temperature has fallen to 1080 degrees Fahr. (930 degrees Fahr. if the deformation has been great). The rate of cooling from the finishing temperature to the lowest temperature at which recrystallization takes place (the germinative temperature) therefore is of great importance in determining the final grain size. In continuous normalizing practice, sheets are cooled from 1750 degrees Fahr. (955 degrees Cent.) to about 1000 degrees Fahr. (540 degrees Cent.) in approximately two minutes.

The grain size is also directly dependent upon the amount of work the metal has received. Dr. Sauveur has graphically shown the resulting relative grain size with varying degrees of working, in Fig. 1. The diagram shows that the grain is smaller and the germinative temperature lower, the greater the deformation.

A. T. Kathner and P. Damiron[2] point out that the greater the difference between Ac_1 and Ac_3, the more chance the ferrite will have to grow upon cooling, since during the cooling the ferrite of the austenite will become free. The faster the cooling, therefore, the finer the grains, and the greater the hardness. Messrs. J. Winlock and G. Kelley have shown, as mentioned in footnote (3), that the stretcher strains which are to be found in those parts which have been deeply stamped are usually found in fine-grained sheets. Fine grains are not desirable for deep stamping, because of the hardness of the sheets which interferes with forming operations, and which wears the dies quickly, as well as because of the accompanying stretcher strains. Therefore, relatively slow cooling, such as is obtained in continuous normalizing, is desirable for certain operations.

A characteristic sheet of 21-gage (0.034 inch) thick extra deep drawing automobile fender stock was used in this investigation. The analysis of the sheet was:

	C	Mn	S	P
End	0.06	0.39	0.024	0.008
Center	0.07	0.41	0.035	0.009

The difference in the analysis was due to the segregation in the ingot. Also the carbon content was slightly lower than was reported on the ladle analysis of the heat, indicating that the sheet chosen represented a position in the lower half of the ingot.

In order to get some idea of the amount of deformation the steel investigated was subjected to, its rolling will be briefly outlined. The bars were handled two at a time in the initial or "breakdown" rolling. Each bar received about five single passes (i.e., first passes). The two pieces were then matched together and rolled as one, receiving three such passes. At this stage the pieces were elongated to approximately two-thirds of the required length. The pieces were allowed to cool and then were pickled, after which they were dipped in a bath of finely divided charcoal and water to prevent sticking in the subsequent rolling. The "breakdowns" were next matched in three pieces, reheated, and then given three or four passes to elongate them to the required length, the three sheets being rolled

[2]A. T. Kathner, P. Damiron, "The Manufacture and Heat Treatment of Auto Body Sheets." Revue de Métallurgie, *Revue Universelle des Mines*, Nov. 1930, Vol. 5, No. 7, April 1, 1930.

[3]J. Winlock and G. Kelley, "Sheet and Strip Steel for Automobile Bodies." TRANSACTIONS, American Society for Steel Treating, August, 1930.

as one. Samples investigated were only processed through the hot rolling operation, and no heat treatment or finishing work had been performed on them.

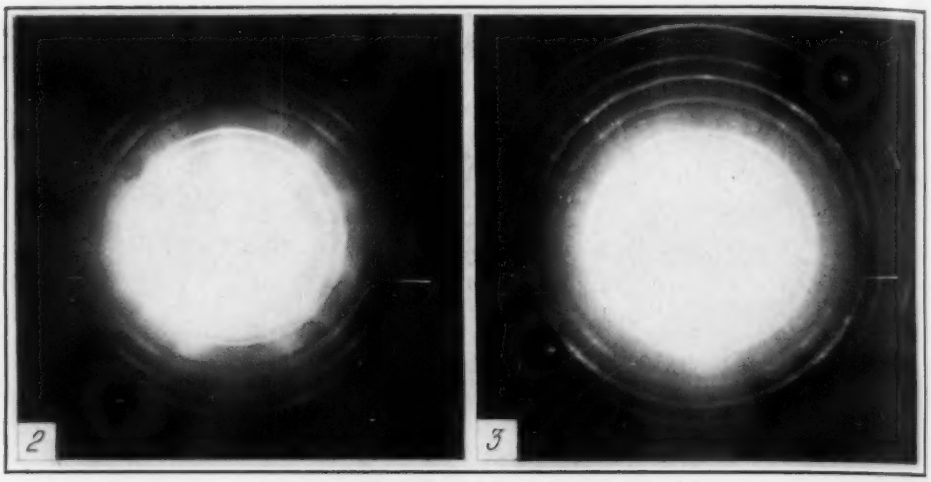
The sheet was cut into middle and end portions. Due to the fact that the X-rays revealed a noticeable difference in the structure of the center and end specimens (Figs. 2 and 3) all samples used were taken from one position in the sheet. In this case, the samples were chosen from the end.

The sheets were then normalized in an electric furnace, the temperature being measured with a platinum, platinum-rhodium thermocouple and potentiometer, and checked with a standard optical pyrometer.

Due to the slowness in heating of electric furnaces, and in an attempt to duplicate actual commercial normalizing operations as closely as possible, as far as the preheating and soaking times are concerned, varying times of preheating and soaking at the various temperatures were carried out, and X-ray diagrams were obtained for each variation. Preheats from three minutes to three and one-half hours were tried; also soaking times varied from one minute to seven minutes. The results of these trials briefly were that the preheating time made no difference in the final structure, while the time of soaking past three minutes gave a slightly larger grain size and further eliminated strains, slightly raising the Erichsen values.

Oxidation of the sheet in the furnace was prevented by pieces of charcoal near the steel. Oxidation during cooling was overcome by constructing a nitrogen cooling chamber into which a small stream of nitrogen was constantly admitted. By means of a differential gage, the nitrogen was admitted at the same rate during all of the coolings. However, it was felt that the cooling which the steel received by this method made the process differ slightly from that of true normalizing. This was later verified by Erichsen values. Hence, in the final work, the samples were removed from the furnace and cooled in air, the resulting scale being removed by easy grinding when necessary. (The scale so formed was rather too thick for a pickling operation).

Later, specimens were heat treated using cover sheets of 18-gage material on top and below to prevent scaling in the furnace and to slow down the cooling. Erichsen values (Table I) show a marked increase over the uncovered air-cooled sheets. The cooling rate was



X-RAY DIFFRACTION PATTERNS
Fig. 2—Untreated Specimen (Center).
Fig. 3—Untreated Specimen (End).

very comparable to that obtained in commercial continuous normalizing.

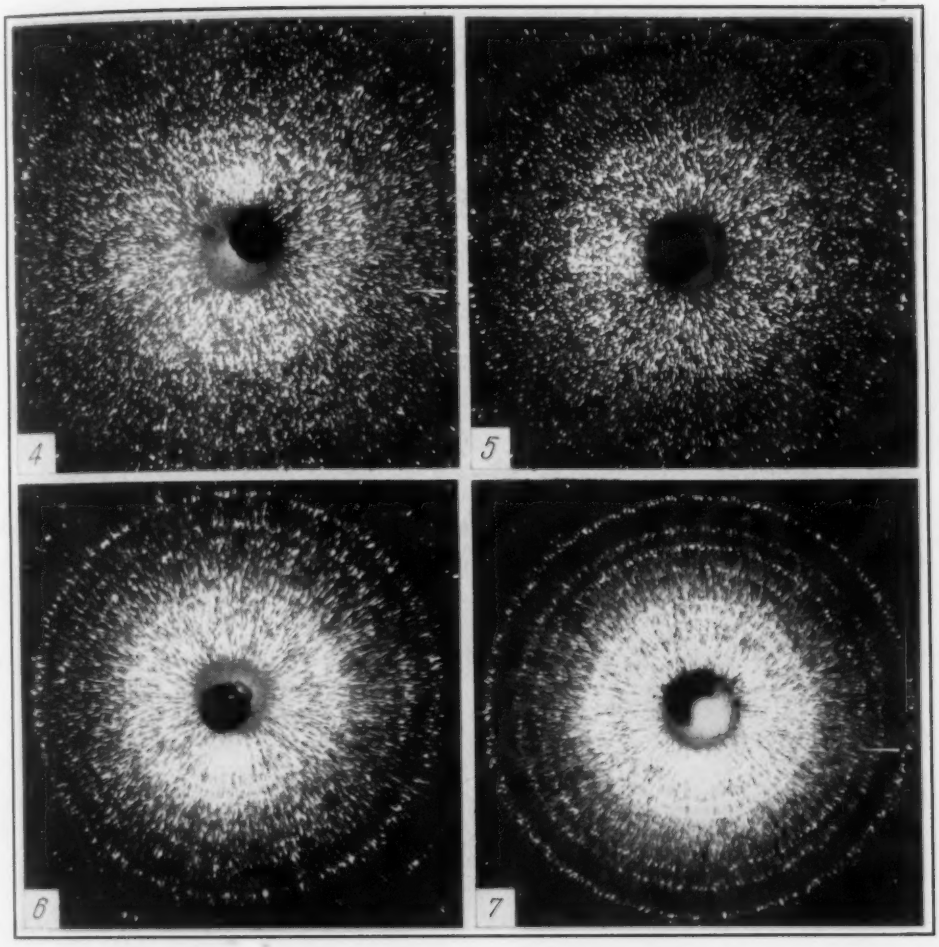
The samples used for X-ray analysis were sheared from the uncovered heat treated sheet and were etched to 0.007 inch in a 20 per cent HNO_3 solution after first removing the scale. The center of the inch square specimen was the portion X-rayed, so as to eliminate any effects of the cold working from the cutting on both sides.

Table I

Erichsen Values
Numerical Results

Sample	(Uncovered Sheets) Value mm.	(Covered Sheets) Value mm.
Unheated (center)	7.43	.....
Unheated (end)	8.01	.....
1450 Degrees Fahr.	9.05	.....
1500 Degrees Fahr.	9.30	.....
1550 Degrees Fahr.	9.53	.....
1600 Degrees Fahr.	9.87	.....
1650 Degrees Fahr.	10.15	10.87
1700 Degrees Fahr.	10.27	11.18
1750 Degrees Fahr.	10.23	11.27
1800 Degrees Fahr.	10.39	11.34

Erichsen values (Table I) were obtained on the various pieces, giving a measure of the workability of the metal. Rockwell tests were made, but the results obtained gave too wide a variation for interpretation, due, most likely, to the thinness of the sheet.

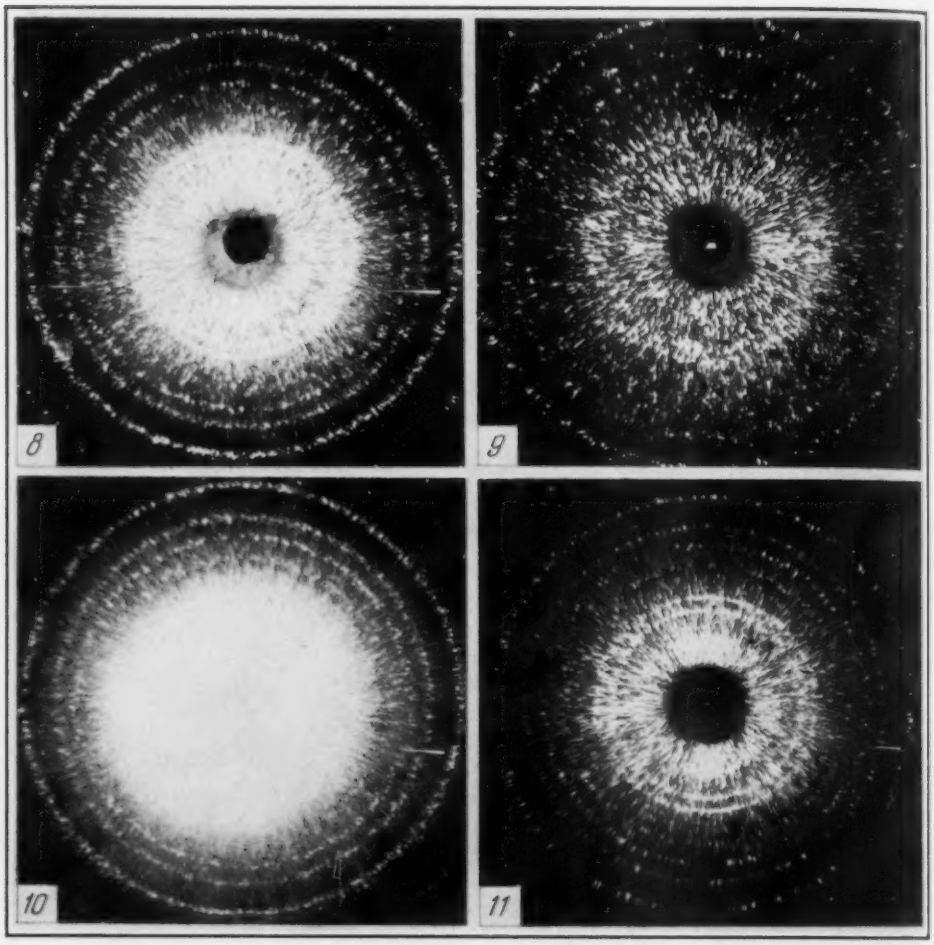


X-RAY DIFFRACTION PATTERNS

Fig. 4—Air-cooled from 1450 Degrees Fahr. (785 Degrees Cent.).
Fig. 5—Air-cooled from 1550 Degrees Fahr. (845 Degrees Cent.).
Fig. 6—Air-cooled from 1600 Degrees Fahr. (870 Degrees Cent.).
Fig. 7—Air-cooled from 1650 Degrees Fahr. (900 Degrees Cent.).

In the X-ray analysis of the specimens, the pin-hole method was employed, using the characteristic radiation of molybdenum. The central undeviated beam was blocked out by means of a lead button so as to register the greatest number of reflections at small angles. The exposure time was forty-five hours. A specimen-to-plate distance of five centimeters was employed.

The specimens herein represented were normalized at temperatures of 1450 to 1800 degrees Fahr., the time of preheating being from four to six minutes with a soaking time in all cases of three minutes.



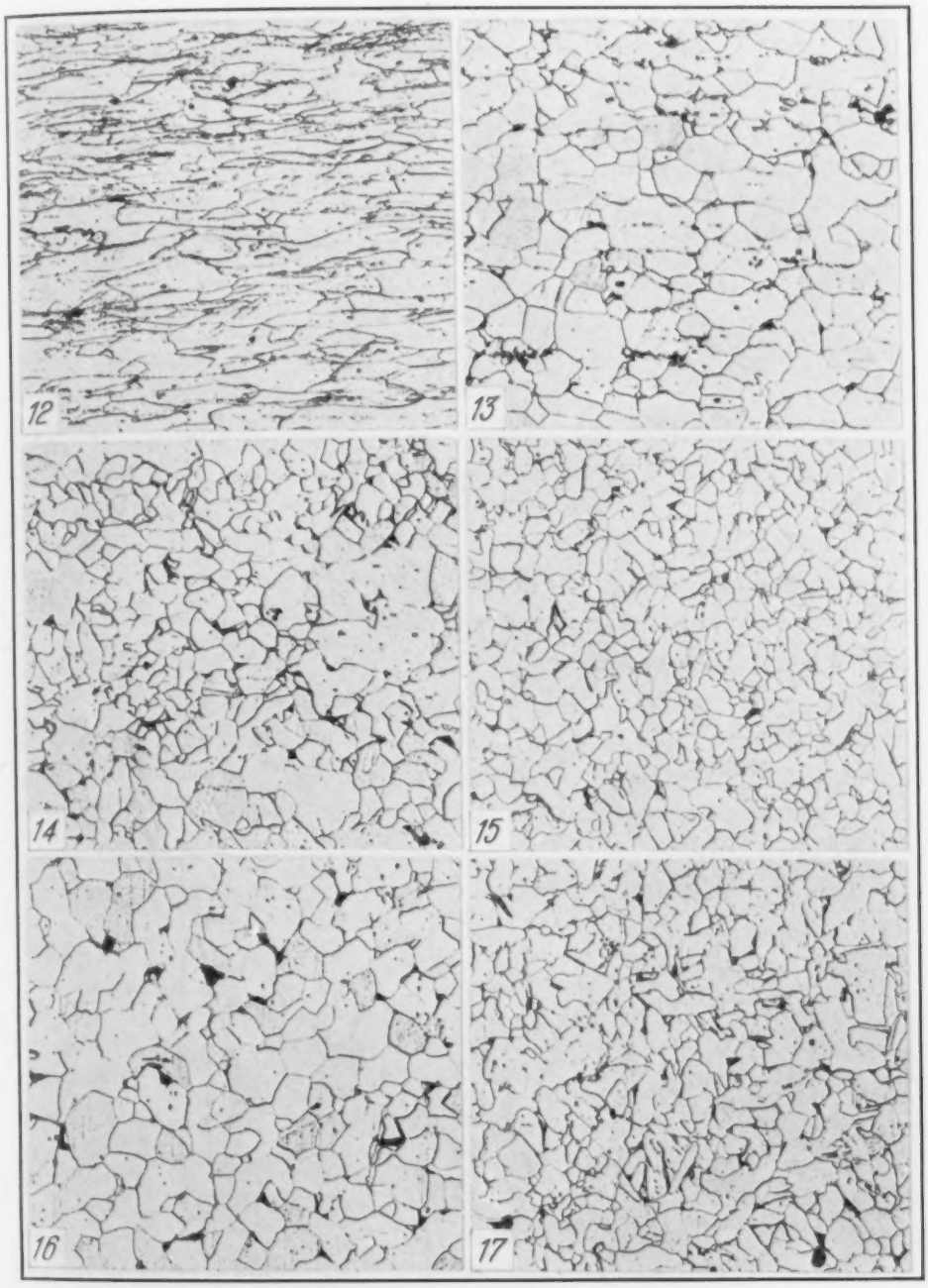
X-RAY DIFFRACTION PATTERNS

Fig. 8—Air-cooled from 1700 Degrees Fahr. (925 Degrees Cent.).
Fig. 9—Cooled with Cover Sheets from 1700 Degrees Fahr. (925 Degrees Cent.).
Fig. 10—Air-cooled from 1800 Degrees Fahr. (980 Degrees Cent.).
Fig. 11—Air-cooled from 1800 Degrees Fahr. (980 Degrees Cent.). Showing Remaining Directional Properties.

Results

In the untreated sample, the difference existing between the end and center of the sheet is evident from Figs. 2 and 3. In Fig. 2, which represents the center of the sheet, it is seen that the internal strains and directional properties are everywhere in evidence, although those in Fig. 2 are more pronounced and of greater intensity than those existing in the end of the sheet (Fig. 3). The internal strains are shown by the "radial asterism" proceeding from the center.

The greater internal strain occurring in the center of the sheet



PHOTOMICROGRAPHS OF SPECIMENS TESTED

Fig. 12—Original Specimen (Longitudinal). × 150.
Fig. 13—Air-cooled from 1450 Degrees Fahr. (785 Degrees Cent.).
Fig. 14—Air-cooled from 1600 Degrees Fahr. (870 Degrees Cent.).
Fig. 15—Air-cooled from 1700 Degrees Fahr. (925 Degrees Cent.).
Fig. 16—Cooled with Cover Sheets from 1700 Degrees Fahr. (925 Degrees Cent.).
Fig. 17—Air-cooled from 1800 Degrees Fahr. (980 Degrees Cent.).

is probably due to the fact that the crystals located in such a position have no direction whereby their strains can be relieved, i. e., they are hemmed in, so to speak, on all sides. In the end portion, on the other hand, the crystals have one direction whereby their internal strains can be relieved.

Directional properties are shown by the "fibering" or intensity spots on the diagrams. The greatly elongated grains are shown in Fig. 12.

Figs. 4 and 5 (1450 and 1550 degrees Fahr.) represent the recrystallizing steel in a strained condition, having a relatively large uniform grain size. Fig. 13 is a photomicrograph of the steel air-cooled from 1450 degrees Fahr. The ferrite grains are equiaxed; however, the sorbite, while broken up, still shows the direction of rolling.

Fig. 6 (1600 degrees Fahr.) indicates that the steel now contains small grains which have formed at this temperature as shown by the formation of the concentric rings. There are still some large grains present, however, as evidenced by the large size of the registrations. The absence of the Debye-Scherrer rings in Figs. 4 and 5 may be attributed to the fact that there is not a large enough proportion of small grains to form such diffraction rings. Fig. 14 shows the large proportion of small grains which are present at 1600 degrees Fahr., corresponding with the diffraction pattern of Fig. 6.

Fig. 7 (1650 degrees Fahr.) shows fine equiaxed grains resulting from the recrystallization at Ac_3. There is a far greater proportion of small grains present at this temperature than was present at 1600 degrees Fahr., as can readily be seen by comparing the size of the registrations, and the increased continuity of the concentric rings, with Fig. 6.

Fig. 8 (1700 degrees Fahr.) indicates that the grains are small and uniform as a result of the recrystallization. Fig. 15 is a photomicrograph of the steel air-cooled from this temperature and shows comparatively small equiaxed grains.

Fig. 9 (1700 degrees Fahr.) is the diffraction pattern of a similar specimen which was heated and air-cooled between 18-gage cover sheets. A larger grain size is noted from the size of the registrations in this diffraction pattern compared to Fig. 8. Likewise, there is no such amount of asterism or halation (signifying strain) in the slowly cooled sheet, as contrasted with Figs. 6, 7 and 8. In the latter figures,

strains were undoubtedly present as a result of the air quenching from temperatures above 1550 degrees Fahr. The smaller amount of cooling strains in the slowly cooled sheets explains, to a great extent, the increase in Erichsen values.

Fig. 16 is a photomicrograph of the steel slowly cooled from 1700 degrees Fahr. A very uniform, equiaxed grain has been obtained which is very desirable for deep drawing operations.

Strains from the rolling have been almost completely removed

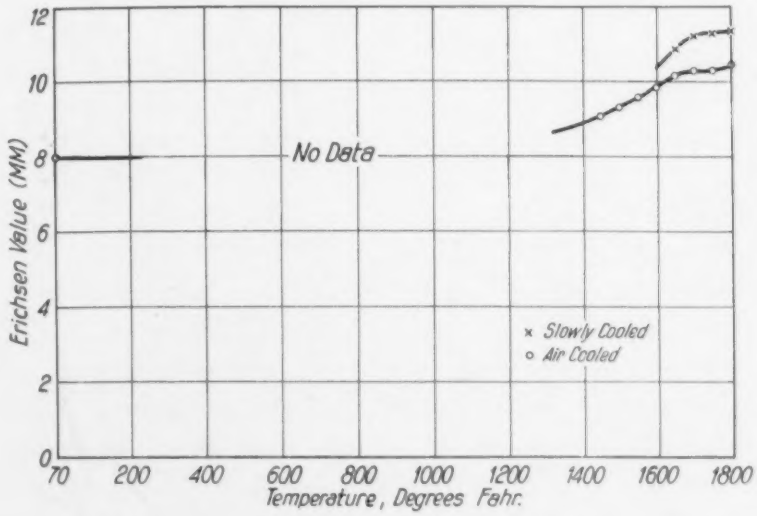


Fig. 18—Effect of Normalizing Temperatures On Erichsen Values.

by the recrystallization above Ac_3. They are not completely removed, however, and Fig. 11 shows the remaining effects by the two intensity spots near the center of the diffraction pattern.

N. P. Goss[4] has pointed out that, although complete recrystallization is effected in annealing a molybdenum wire, directional properties still remain after weeks of heat treatment.

Fig. 10 (1800 degrees Fahr.) contains a considerable amount of quenching strains. The grain size appears to be about the same as that of Fig. 8, but the halation masks the pattern to such an extent that definite comparisons would be unreliable. Fig. 17, a photomicrograph of this specimen, shows the grain size to be too large and unsuitable for deep drawing operations.

Referring to the curve of Fig. 18, based on values given in Table

[4]N. P. Goss, "Application of X-rays to the Study of Plastic Deformation in Steel Wires and Molybdenum Ribbon," TRANSACTIONS, American Society for Steel Treating, Vol. 17, February, 1930.

I, it is seen that the Erichsen values for the sheets increase steadily, the sheet becoming softer the higher the normalizing temperature. Slower cooling decidedly improved the workability of the steel.

Since between 1700 and 1750 degrees Fahr. an Erichsen value well within the usual standard for 21-gage, extra deep drawing sheets is obtained; and since the microstructures and X-ray diffraction patterns for both the air-cooled and slowly cooled sheets were very satisfactory; it is concluded that 1700-1750 degrees Fahr. is best suited for normalizing such sheets.

Summary of Results

1. A temperature of 1700 to 1750 degrees Fahr. was found by photomicrographs, X-ray patterns, and Erichsen values, to be the most favorable temperature for normalizing operations.
2. Slower cooling, effected by cooling the sheets between 18-gage cover sheets, gave an increase of approximately 10 per cent in Erichsen values. The grains remained small and the rupture of the Erichsen cup was almost completely circular.
3. The X-ray diffraction pattern of the slowly cooled sheet showed a much more desirable pattern for deep drawing operation than did a similar sheet air-cooled.
4. Increased preheating period had no effect on the structure.
5. Increased soaking time at temperature gave slightly higher Erichsen values.

Acknowledgment

The author is indebted to W. R. Williams of The Youngstown Sheet and Tube Company, who proposed this subject for study. He is also grateful to the members of the Department of Metallurgy, Lehigh University, for their cooperation, and especially to Prof. H. V. Anderson, whose advice and direction was greatly appreciated.

DISCUSSION

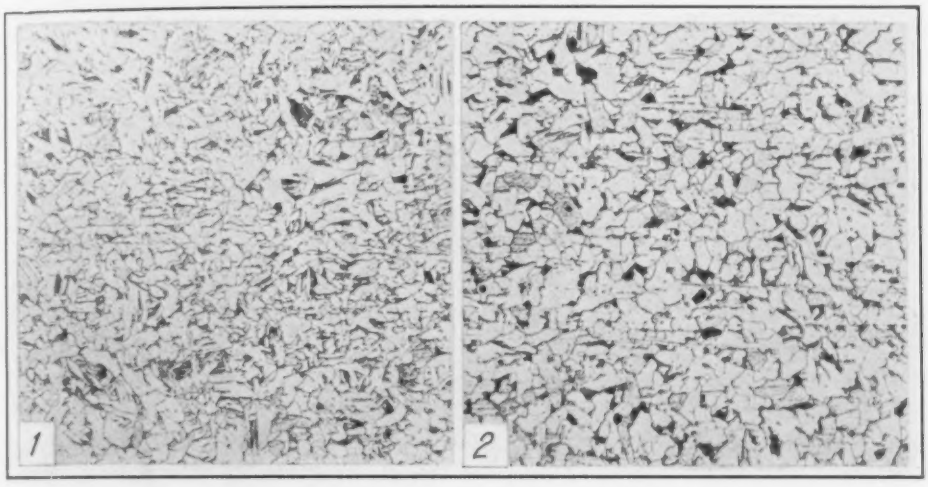
Written Discussion: By Thomas Dockray, metallurgist, Eastern Rolling Mill Co., Baltimore.

In discussions upon these papers we are taking every opportunity to discuss any debatable point presented, as we feel that there are many of these, known and unknown. By this means it is hoped that a lively interest will be maintained in these subjects prompting more and more sessions of this character.

In the beginning of this paper the term and definition of normalizing are

used. The first furnaces for normalizing were correctly named, for in this case the sheets emerged from the furnace into the air from above the critical temperature. However, the latest type of furnace has a cooling zone of say 50 feet in length subsequent to the normalizing zone, the effect of which is to gradually reduce the temperature of the sheet to about 1300 degrees Fahr. when it comes into contact with the air and is quickly cooled. Can we then apply the term "normalizing" to this operation?

The original type of normalizer is still in use and because of this fact the assertion that the purpose of normalizing is to obtain equiaxed grains among



other things, when applied to the usual thickness of sheet made, is hardly correct. A fairly equiaxed grain can be obtained with a very low carbon sheet (0.04 per cent carbon) on air quenching, but with say 0.10 per cent carbon the structure is different; in this case a martensitic influence can be seen in the long grains. (Fig. 1.) The same type of sheet normalized at the same temperature in a furnace with a cooling zone which allows time for a readjustment of the structure by the slow cooling, has a more equiaxed grain, the extent depending upon the rate of cooling. (Fig. 2.)

However, with a furnace without a cooling zone the structure with a 16-gage sheet will be different from that of a 20-gage sheet because the extra thickness slows down the rate of cooling which has its effect upon the structure, which approaches more to an equiaxed type.

The term normalizing was conceived in relation to material of appreciable thickness but the generally stated effects are not accurate when considering the lighter gage sheets where, instead of a slow air cooling from the upper critical, there is a quenching action. In like manner when cooling is performed in a cooling zone the definition does not pertain to the process; it would seem that a new term is necessary which will convey a better idea of the actual cycle performed and results obtained to the mind of one not familiar with the process.

It is stated that "fine" grains are not desirable for deep stampings because of the hardness of these sheets. In the first place it would be interesting to know the magnitude of a grain called a "fine" grain. A normalized grain

contrasted to some large grains obtained in box annealing can be called a fine grain, and yet many box-annealed sheets by proper rolling and annealing conditions can approach the fineness of a normalized grain. Of course normalized grains can be obtained in different sizes showing a bigger contrast than as shown in Figs. 1 and 2 but it is the writer's opinion that this difference of grain size shows very little difference in the intensity of stretcher strains.

As explained by Winlock and Kelley in the article referred to, with a large grain there are wider, local depressions formed at the yield point than with a fine-grained sheet due to the greater heterogeneity of the gliding planes in the latter and consequently a greater number of separate areas of slip per unit surface area. The difference is in the number of strained areas but not in the total amount of strain deformation. In our opinion stretcher strains in a normalized sheet or even a box-annealed sheet of a good grain structure are a function of the amount of plastic deformation produced in a sheet by cold work previous to stamping and not of the grain size.

Greater hardness is ascribed to a fine grain. This may be so if the two types have been submitted to identical processing but it is generally found that a plant will standardize upon a certain range of grain size and annealing is performed in order to obtain the maximum softness in this sheet. The decrease in hardness obtained by annealing is not obtained by grain growth but by eliminating the effect of the relatively quick cooling from the normalizer.

The two types of grain structure shown in Figs. 1 and 2 are produced regularly at the plant of the writer, but with practically the same annealing, the same hardness values and performance are obtained with a cold-rolled last sheet.

In the treatment of the specimens they were removed from the experimental furnace and cooled in air and this operation sometimes caused a scale too thick to be removed by pickling. This method and the physical characteristics found could hardly be deemed analogous to those found after a sheet had traversed a normalizer with a cooling zone. In our experience the air quenching and the cooling zone normalizers produce different physical properties in the same sheet. And could this difference in cooling not be included in the X-ray patterns?

In the X-ray examination samples were taken from the end of the sheet—would this give an accurate conception of what happened in the center of the sheet? Moreover would these samples apparently from the bottom of the ingot give the same reaction as samples from the top of the ingot where segregation would be pronounced?

The samples were small and the deductions arrived at were from a stationary condition in a small furnace. It is hardly possible to apply these deductions to sheets of much larger dimensions passing through an enormously larger production furnace. Has the author ever watched the progress of a sheet through a normalizer and observed that parts of the sheet heat quicker than others, so that even in the normalizing zone a spotty condition can be seen with the areas varying as much as 50 degrees Fahr. and more? Personally I prefer to do my experiments with a full sized sheet going through the regular process, as I am convinced that true deductions cannot be obtained

from a laboratory furnace whose size is infinitesimal compared to the production furnace.

Deductions have been made from several samples taken from a "characteristic" sheet. This word prompts the question as to what is a characteristic sheet. These sheets are made in packs of three and it is patent that the middle sheet has different properties after rolling to length than the outside sheet, because this sheet retains the heat longer than the outside sheets and so is hardened to a different extent by the rolling. Because the germinative temperature of the new structure varies with the amount of stress put into the steel it occurs to me that the X-ray would show that an outside and an inside sheet of a pack would respond differently to the normalizing. It would be interesting to know if the author has any information in this respect.

Written Discussion: By H. M. Cox, metallurgist, Michigan Steel Corporation, Detroit.

The use of X-ray examination will without doubt bring to light many of the reasons for nonuniformity in drawing quality of flat-rolled products. To bring its full value to the attention of those interested we suggest a paper by these authors showing samples of identical microstructures where a marked difference is shown by the X-ray.

We check very well the proper temperature for normalizing, 1700 degrees Fahr. being the low limit for satisfactory results and feel a slightly higher temperature, say near the upper limit shown in the paper, to be much safer in practice.

In regard to preheating having no effect on final grain size this of course depends on the preheating and also the normalizing. Where analysis is known within narrow limits and cycle can be controlled as in a laboratory furnace no doubt little effect will be shown by preheating except in case of very low carbon material, but in case of commercial normalizing furnaces where conditions are usually such that size of grain is more or less set for average conditions, the condition of material before normalizing does affect final grain size. However, since to produce such a condition actual grain growth is necessary in preheating, the authors are right as far as present normalizing is concerned.

Written Discussion: By R. L. Kenyon, supervising research engineer, American Rolling Mill Co., Middletown, Ohio.

This paper shows the progressiveness that is being evidenced on the part of sheet manufacturers in applying modern tools such as X-ray studies to the problem of producing deep drawing steel sheets. There are some statements in the paper, however, with which the writer is not in entire agreement.

Contrary to the statement on page 141, a sheet temperature considerably below 1750 degrees Fahr. will eliminate strains due to rolling if the amount of cold working is sufficient. To accomplish the A_3 transformation it is necessary to go somewhat above 1650 degrees Fahr. but this depends on the rate of heating, or perhaps more accurately stated, it depends on the time above 1650 degrees Fahr. In continuous furnaces it is necessary to raise the sheet temperature to about 1750 degrees Fahr. in order to accomplish this transformation because of the short time of heating.

It is unfortunate that specific reference to source was omitted in connec-

tion with Kathner and Damiron's reported findings in regard to the difference between Ac_1 and Ac_3 affecting grain size.

Written Discussion: By Wilber E. Harvey, department of metallurgy, Lehigh University, Bethlehem, Pa.

It would seem after reading this paper that again the successful use of the X-ray in metallurgical problems has been proven. The results obtained by Messrs. McGarrity and Anderson by X-rays seem to corroborate their metallographic and physical tests very nicely, and substantiate that the X-ray can be made a valuable adjunct to the metallurgists' equipment. Not only does the X-ray analysis agree with the microscopic revealings in this paper but the X-ray digs one bit further into the internal properties of the sheet steel under study. While all the strain and directional properties seem by a microscopic study to have been removed by a 7-minute normalizing at 1800 degrees Fahr., as shown in Fig. 17, the X-ray reveals that the directional properties caused by rolling have not entirely disappeared. That the X-ray should develop such results which the microscopic examination fails to reveal is not surprising when it is considered that the X-ray examines the actual finite internal structure comprising the material while the microscopic examination is a surface examination. It is from this standpoint that the two methods of examination in conjunction with each other form such a valuable series of tests. While at present this piece of information concerning directional properties may have no absolute commercial value, it is a valuable piece of knowledge to possess. The paper seems to be of scientific interest only, yet it certainly impresses that the combined use of metallographic and X-ray equipment forms a powerful aid to the modern laboratorian.

Authors' Closure

We are hesitant about even attempting to suggest a more explanatory term for such a normalizing process as is mentioned in Mr. Dockray's excellent discussion, yet we fully agree that one is needed to convey the impression of a slower cooling. "Continuous Normalizing" seems to contain some inkling that the cooling is not as fast as an air quench; however, if the authors might suggest a more explanatory term, it would be "Normannealing." Perhaps this would convey the desired impression of slow cooling from a temperature exceeding the critical range.

Rates of cooling from different temperatures have quite a noticeable influence upon the X-ray patterns. Fig. 9, made shortly after the preprint was published, illustrates this effect. The grains are larger and more equiaxed when the specimen was slowly cooled, and the internal strains which were set up in all specimens air-cooled from above 1550 degrees Fahr. were completely obliterated by the slower cooling.

As yet, we have no definite information as to whether or not samples from the bottom of the ingot give the same reaction as samples from the top.

It is unfortunate that it was not possible to carry out the experiments on a large scale as is mentioned; however, we believe that an averaging of different pictures made on samples selected from similar sheets and treated even in a small furnace will show a definite trend, and basic information obtained from these observations could then be verified by a large scale test.

PLASTIC DRAWING OF SHEET STEEL INTO SHAPES

By E. V. Crane

Abstract

Extreme plastic movement or rearrangement of metal (cold) is illustrated in drawing round shells. Principles developed there may be applied also to rectangular and irregular shapes. The primary stress is the tensile stress in the shell wall which is rarely in the necking range and often below the yield point. The resultant compressive stress in the flange area during drawing must always exceed the annealed yield point and often rises to necking range stresses well above the nominal ultimate tensile strength. The extensive metal movement in this area causes strain hardening of the crystal structure at a predictable rate. Press operations and drawing operations in particular, require development of plastic working theory and physical properties which describe the metal above its annealed elastic limit. Such data assist in explaining the troubles met with and the limitations upon drawing operations.

WE know that drawing operations were being performed on sheet metal near the middle of the last century. A design for a drawing press employing weights for blankholding is said to have been brought from France in 1860. Double action presses using cams for the blankholding function appeared in the catalogs of two or three of the young press companies in 1872.

The great bulk of our drawing operations are performed cold and involve extensive rearrangement of the metal structure. This plastic movement occurs, of course, entirely beyond the elastic limit, or yield point, of the metal and is carried on well into the necking range of the tensile test, and often practically to the point of stress represented by the fracture at the neck in the tensile test. We are inclined to believe at present that valuable concepts and data with reference to drawing operations may be developed from further investigation of certain theories of plastic working. We will en-

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A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, E. V. Crane, is staff engineer with the E. W. Bliss Co., Brooklyn, N. Y. Manuscript received June 20, 1931.

deavor to review briefly first the manner in which the metal is moved in drawing operations and then the troubles which appear in the production of drawn parts with reference, where necessary, to the plastic working theories.

Plastic Movement in Drawing

The drawing of a round shell is the best starting point for an analysis as it involves entirely balanced stresses. Thus, Fig. 1 shows such a shell partially drawn through in tools which are cut away to

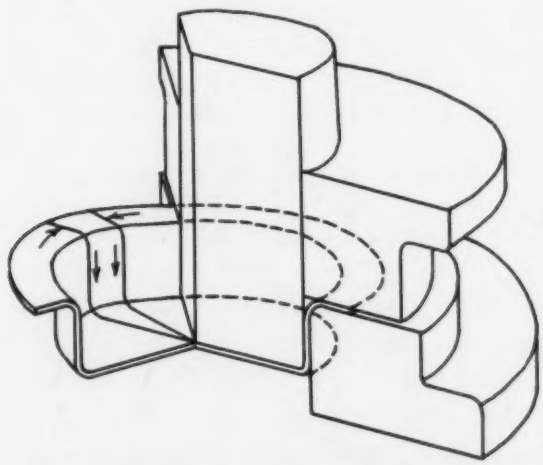


Fig. 1—In Drawing from a Flat Blank to a Cylindrical Shell, the Metal is Rearranged in the Flange Area by Plastic Cold Working with Accompanying Strain-hardening.

show their action. The blankholding ring holds the flat blank or disk against the surface of the die to prevent the formation of wrinkles while the punch descends to draw the metal into a cylindrical shell.

If, before starting the draw, two straight lines had been drawn upon the flat disk spreading at an angle of about 15 degrees from its center, they would now appear as indicated by the lines marked with arrows. In the bottom of the shell they show that the metal has not been disturbed. In the side wall they have become parallel, indicating the greater and greater distortion as we proceed up from the bottom of the shell. In the flange they maintain their original angular relation but are drawing closer and closer together as the flange is drawn in and its circumference is reduced. Obviously, the most severely worked metal is that around the outside periphery of the blank which has been rearranged so that the circumference has

become in the shell perhaps a half of what it was in the blank.

The movement of the metal which the lines indicate suggests the stresses involved. The vertical arrows denote the tensile stress in the side wall of the shell which is due directly to pressure of the drawing punch against the bottom of the shell. The two arrows on the flange indicate the crowding, or compressive stresses set up in that area as the circumference of the blank continues to be reduced. It is this induced compressive stress in the flange which must exceed the yield point before rearrangement of the metal begins and which is directly responsible for the actual metal movement. The compressive stress is, of course, a resultant of the tensile stress over the drawing edge, and, as the flange becomes narrower and narrower, the tensile stress becomes proportionately lower. Our tests indicate, for example, that, in an extremely low shell, the tensile stress in the side wall may be materially below the annealed elastic limit.

Fig. 2 illustrates, by way of example, the distortion of metal in drawing a rectangular shape. The original blank at the right is rectangular in shape with the corners sheared off on a radius. Reference to the drawn shell at the left will show that the sides of the shell have been pulled in along reasonably parallel lines in the central part of the shell. As a matter of fact, we find that this metal has been subject only to the plastic working involved in bending over the corner radii. Except in a few cases where shapes are shallow, the metal is not pinched hard and is not subject to either stretching or squeezing together along either the vertical or horizontal center lines. The corner area would seem to be directly comparable to round drawing work in which very considerable compressive rearrangement in the flange is necessary. For practical purposes, this is the case, but not quite the same stress intensities are involved as a certain amount of the surplus metal is moved out into the adjacent straight portions of the side where there would otherwise be no compressive stress. This nonuniform distribution of stresses in the flange of the shell where the plastic rearrangement is taking place is naturally a source of possible trouble, especially with reference to the formation of wrinkles.

The Tendency to Wrinkle

This tendency to form wrinkles at various points in a drawn shape is one of the principal troubles encountered in drawing opera-

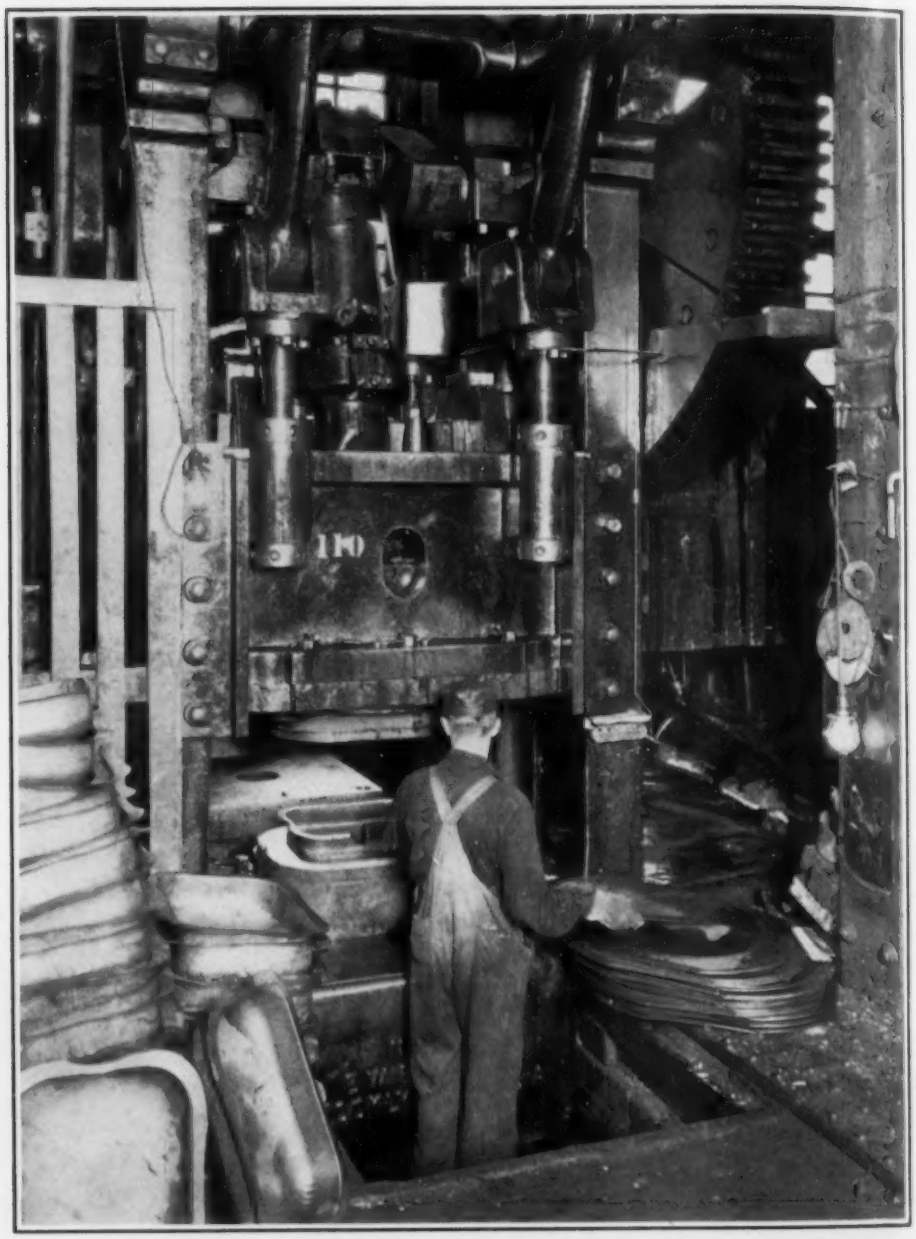


Fig.2—In Drawing a Rectangular Shape, the Compressive Stresses which Reshape the Metal are Localized in the Corner Flange Area.

tions. Fig. 3 is arranged in an effort to show why wrinkles form in the flange of a shell which is being drawn. Two positions of the same volume, or section, of metal are shown in plan at "a," in section at "b," and in an edge view of the flange at "c." The dotted lines indicate the original position at the start of the draw while the solid lines

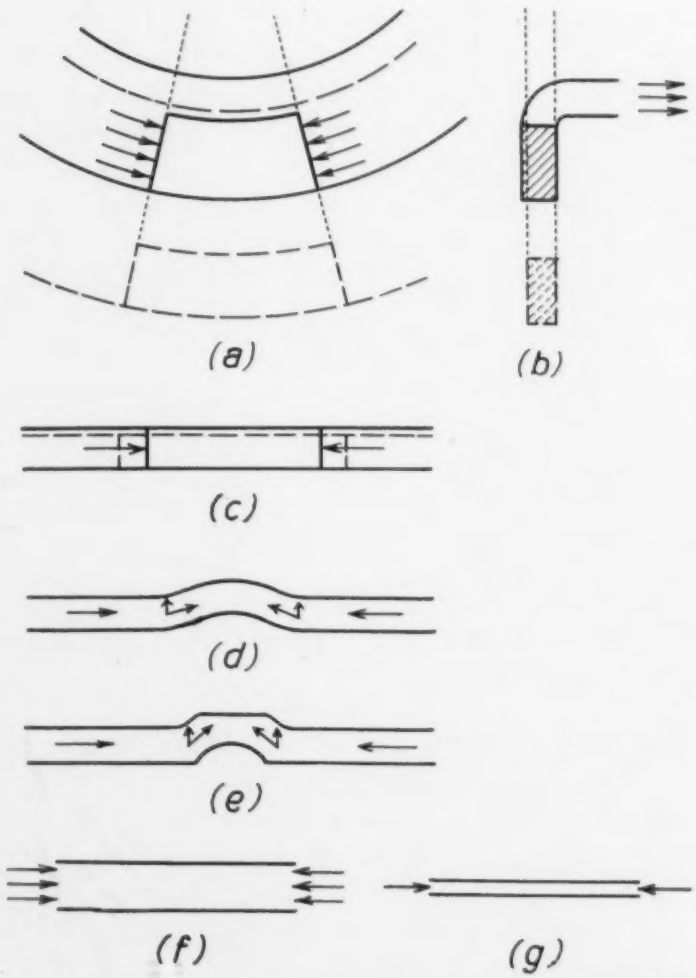


Fig. 3—Rearrangement of the Same Volume of Metal (dotted to solid positions) in a Shell Flange (a,b,c); Wrinkle Formation and Up-thrust (c,d,e); Advantage of Relatively Thick Material in Resisting Buckling (f,g).

show the position with the draw approaching completion. The arrows in views "a" and "c" indicate the compressive stresses (above the yield point) which must be developed in the flange to compress the metal into the progressively smaller circumference. The arrows in view "b" indicate the tensile stresses in the side wall which may be considered to be pulling the metal into a narrower and narrower wedge-shaped space, as indicated at "a."

The condition at "c" may be compared with that in a structural column which is loaded beyond its elastic limit and is gradually being squeezed down plastically. If the column is thick and short, as at "f," it may become thicker and shorter without buckling. That is the

condition found in trying those brake drums and first-operation hubs (see Fig. 4) where the metal is so thick relative to the diameter and depth of the shell that no blankholding pressure is required.

On the other hand, if the column is long and thin, as at "g," it will undoubtedly buckle and bend to one side under the load, though the load per unit of area is no greater than in the previous case.

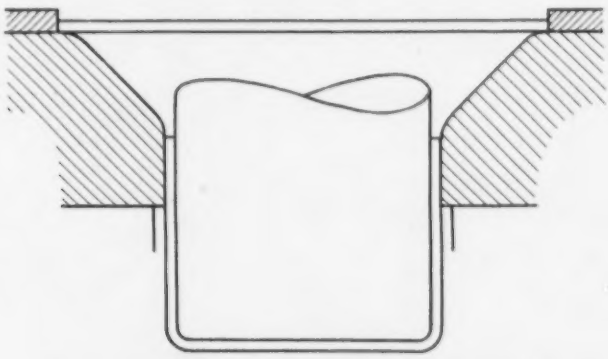


Fig. 4—A Blank Which is Sufficiently Thick Relative to its Diameter to Preclude Wrinkling may be Drawn Without a Blankholder.

This parallels those relatively thin blanks which must be held flat to prevent buckling under compressive stresses.

The initial buckle, or wrinkle, is due to some lack of uniformity in the movement or resistance to movement in the cross section of the metal. The plastic movement in the individual crystal takes place by an angular slippage. It may therefore be seen that a large crystal or group of crystals of especially favorable orientation, may reduce the resistance locally on one surface of a blank or on one side of a column and tend to cause a buckle, or wrinkle, toward the other side. A blankholding pressure sufficient to resist or compensate for this nonuniform movement would prevent the buckle.

Once the wrinkle starts, the perpendicular component of the compressive stress increases rapidly, as shown at "d" and "e"; also, the growth of one wrinkle tends to raise the blankholder from the surface of the metal so that others can form more easily.

It is possible that the reason for the reduced tendency to wrinkle in such single action drawing jobs as that illustrated in Fig. 4 and Fig. 3-f is that the metal is so thick relative to the average grain size that nonuniformities in the distribution of large and small grains, or of grains of varying crystal orientation, are averaged out so that the stresses are practically uniform. Single action drawing and redraw-

ing describes operations in which no blankholding function is required as compared with double action drawing and redrawing where a blankholder becomes essential to prevent the appearance of wrinkles.

Fig. 5 shows a chart prepared tentatively from existing data as a means of using the relation between the metal thickness and the diameter of the blank, or the previous shell in the case of redrawing, to determine how much of a reduction may be made in single action

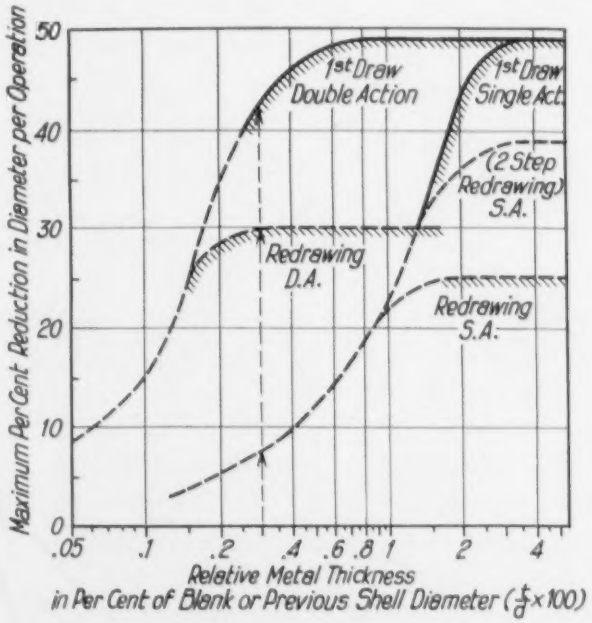


Fig. 5—Tentative Limits Upon the Maximum Reduction, Single Action or Double Action, in Drawing and Redrawing Based Upon the Relation of Metal Thickness to Diameter of Blank or Previous Shell.

or double action tools without causing wrinkles. Such a chart is quite empirical, and as comparatively few data have been collected with specific reference to arranging such a chart, alterations in it may readily be possible. It is suggested that those interested plot as a point on this chart the relations between metal thickness, initial blank or shell diameter, and per cent reduction for the various jobs going through their shops.

The foregoing refers to the tendency of metal to wrinkle in the flange during drawing. A similar tendency to wrinkle is found in the side walls of shells being drawn from a flat blank directly into a tapered shell. This is because the inside diameters of the blankholding and drawing rings are determined by the largest diameter

of the taper whereas the metal is being drawn down by the nose of the punch, which is equal in diameter to the small end of the taper. There is, then, a considerable area in which compressive reducing stresses are created similar to those occurring in the flange, but without any possibility of a blankholding action to make the metal upset rather than buckle. If, then, the metal is thin relative to the width of the unsupported area, wrinkles are practically certain to occur. For that reason, many tapered parts are drawn first to a stepped profile of smaller diameter than the taper and then expanded, or stretched, on the nose of a drawing punch into the tapered shape, as in the stretching operation there are no wrinkle-forming stresses.

It may be noted also that, at the beginning of any drawing operation, there is an unsupported area of blank from the outside edge of the radius on the draw die to the inside edge of the radius on the nose of the drawing punch. As these radii are usually relatively small, this total distance is also relatively small compared with the metal thickness and the tendency to wrinkle is negligible. Cases are found, however, in which the radius on the nose of the punch, for example, may be considerable and the metal is relatively thin, with results that wrinkles will form. Whenever wrinkles of any sort form in any drawing operation, it is practically impossible to remove them entirely. They may be flattened down in a stamping operation, or pounded out by hand, but it is usually much simpler and more effective to so arrange the operations that the wrinkle may be prevented from forming.

Fig. 6 suggests another class of wrinkle formations which is really related, however, to that just described. In many irregularly shaped drawing operations where there are reverse curves as in the fender shown, conditions may be found which may not be avoidable wherein some portion of the metal is subject to movement in compression over an area where blankholding to prevent wrinkles cannot be arranged. More often, however, it is possible to so design the blankholding surfaces with relation to the drawing profile that the metal which cannot be held flat between blankholding surfaces is always in tension over a punch or pad surface.

Metal Surface Markings

A number of distinctly different markings are recognizable on the outer surface of drawn shells to indicate what has been done to

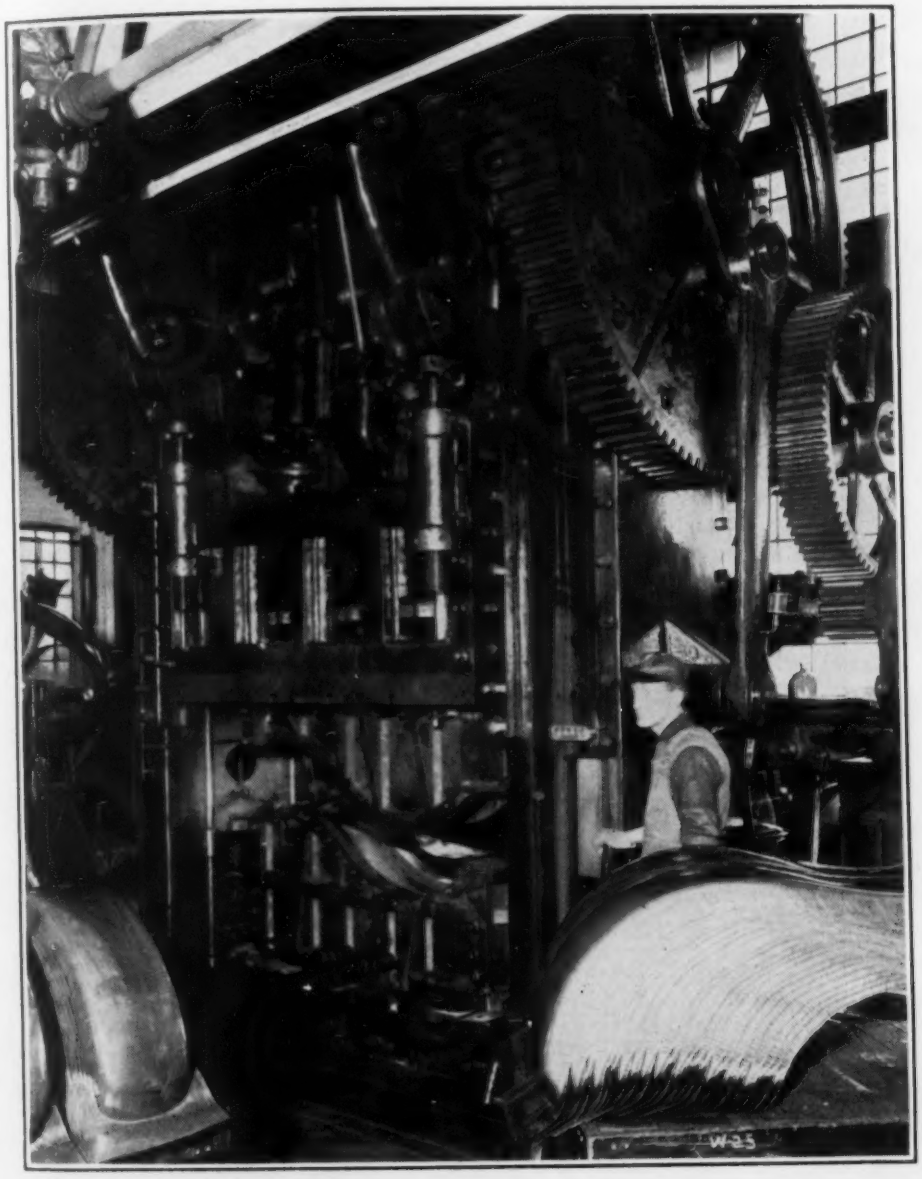


Fig. 6—In Drawing Shapes Including Tapers or Reverse Curves, as in the Production of Fenders, an Area of Metal Subject to Compressive Internal Stresses and not Restrained Between Blankholding Surfaces, is Likely to Cause Wrinkles Unless it is Thick Relative to the Unsupported Area.

them. Thus, a burnished or polished outer wall surface indicates ironing, or reduction in wall thickness by using a clearance between the drawing punch and die which is less than the metal thickness. If the polish extends only part way down the shell, the clearance between punch and die is probably about equal to the original metal thickness

and the ironing is merely the removal of that natural increase in thickness due to drawing. Ironing to remove pits due to pickling or tumbling, or to burnish the whole length of the side requires a die clearance considerably less than the original metal thickness and a relatively low drawing speed (for steel, say, 20 or 25 feet per minute). Ironing will also burnish over surface cracks but will not remove the weakening effect of their presence.

Vertical surface scratches indicate that metal has picked up, or welded, on the drawing radius of the die. The cure may be repolishing the ring, or using a harder ring or a ring of some other metal, or a better lubricant, or it may be that the press must be slowed down. A considerable collection of data indicates that, under normal conditions, picking up on the die is almost unavoidable at actual drawing speeds in excess of 50 or 60 feet per minute of drawing velocity. Differences in lubricant, drawing radius, metal thickness, die material, and cleanness of the metal surface will affect this speed limit to a certain extent.

Vertical cracks frequently start down from the raw top edge of the shell if the particular metal is being cold-worked excessively between anneals. The cure is usually more frequent annealing, less severe reduction, or better material. If the cracks do not appear until hours or weeks after drawing, the phenomenon is called season-cracking. The causes are the same but the action may be aggravated by traces of unremoved pickling acid. This acid, particularly in moist atmosphere, is said to react to free hydrogen which is absorbed by the metal and seems to lower the atomic cohesive strength along the grain boundaries and make the metal brittle.

Frequently, the surface of bright-finished stock will show evidences of the internal working which the metal has undergone. Thus, over a corner radius and up the side, the surface may change to a dull finish with the appearance of a pebbled surface or a series of tiny bumps under magnification. Here a relatively limited internal movement has apparently been sufficient to cause a twisting of groups of crystals through slip plane movements.

Extremely severe cold working of the metal will often produce a shell wall showing many minute fractures on its surface. This is an indication that too great a reduction is being taken between anneals or that the metal being used strain-hardens too rapidly for the particular operation, which, of course, amounts to the same thing. The plastic working of the metal has been carried to such a point that all

available slip planes have been used up and fractures are beginning to occur both on the surface and in the internal structure. Such fractures cannot be removed by any annealing process.

Reference should also be made to stretcher strains, or alligator skin markings on the bottom of the shell or on such shallow jobs as that shown in Fig. 7. This illustrates a cross section of the operation in drawing a casket top or vault top. Many automobile body operations fall into the same class, as the metal must be pinched very tightly

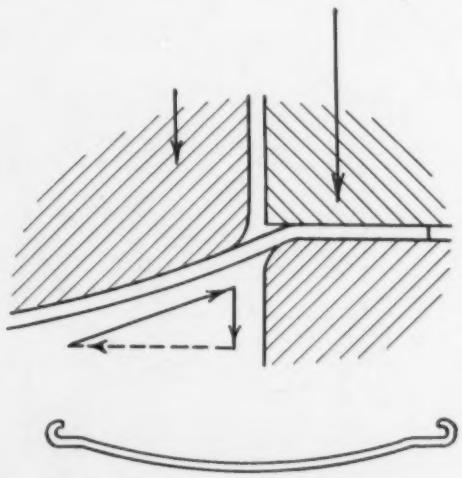


Fig. 7—A Relatively Low Drawing Pressure but High Blankholding Pressure is Required in Stretching a Shallow Shape.

around the flange and stretched slightly beyond its elastic limit to make it hold its shape. When such metal has a high surface finish and yet is very soft and free from strain hardening, the slight movement of the metal involved may not be uniformly distributed over the whole area, but localized along lines which leave patches and irregularly shaped spaces untouched. The most effective cure for this trouble appears to be to run the sheets through a roller leveller or straightener to strain harden them a small but uniform amount just before the drawing operation is performed. Other surface markings due to appearance of wrinkles which are subsequently ironed out to a considerable extent, and wrinkles due to short radii, etc., are more or less obvious and need not be discussed.

Shell Breakage and Reductions

Shell breakage by tearing the bottom out is usually traceable to

an excessive reduction. Referring back to Fig. 1, it is a case of too wide a flange, or perhaps too severely strain-hardened a material, so that the tensile stress in the shell wall exceeds the stress at which necking is likely to occur in the tensile test performed at equal speed. Breakage may also be hastened in such a case by die construction on previous operations, especially the use of too small a punch radius on

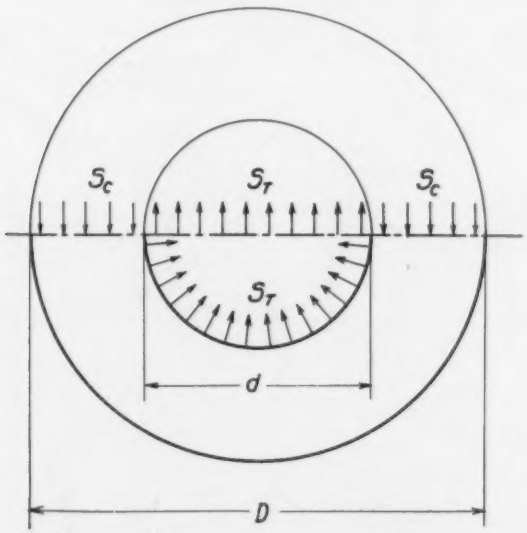


Fig. 8—The Circles Representing Shell Diameter and Blank Diameter; Compressive Stresses in the Flange Area Exceeding the Yield Point Cause Equal Total Tensile Stress Projected Along the Same Cross Section Line.

a previous reduction so that the metal has been unduly thinned out at the corner. Fig. 8 has been arranged to illustrate the relation between compressive stresses in the flange and tensile stresses in the wall according to the relation between blank diameter and shell diameter. An experimental confirmation of this theory is offered in the curves shown in Fig. 9. Referring to Fig. 8, assume that "D" indicates the blank diameter and "d" the shell diameter and represent along some line through the centerline of the shell the compressive stresses occurring in the flange designated "S_c". The resultant tensile stresses over the drawing radius are represented by radial arrows "S_t". It has been shown mathematically that the component of these radial forces along the cross section line is equal to the unit tensile stress times the small diameter; that is, the total compressive stress may be expressed as $S_c \times (D\text{-}d)$, and the total tensile stress projected along the same section line may be expressed as $S_t \times d$. As the tensile

stress over the radius is the resultant of the compressive stress in the flange, we may equate the two expressions and give the value

$$S_t = S_c \, (D\text{-}d) \, / \, d.$$

To this we add an allowance for bending the metal over the die radius and for friction losses under the blankholding surface in the development of the formula for drawing pressure. This develop-

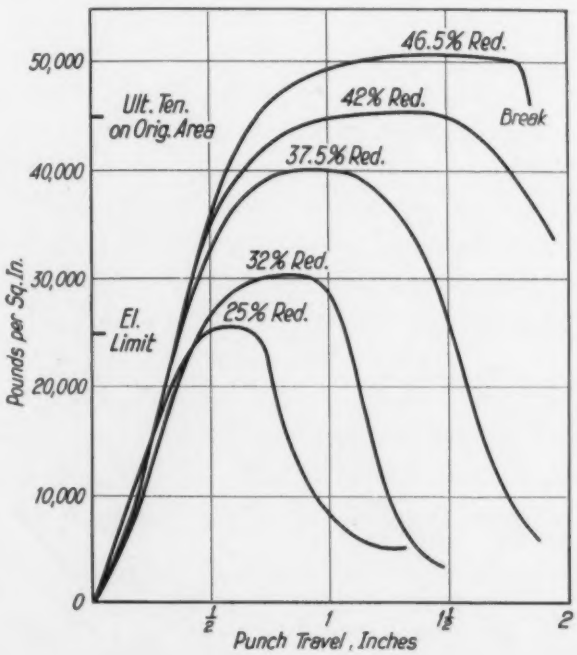


Fig. 9—Effect Upon the Unit Stress in the Shell Wall of Drawing 5, 5½, 6, 6½, and 7 inches in Diameter Blanks Into 3¾-inch Diameter Shells. Compare with Elastic Limit and Nominal Tensile Strength of the Metal.

ment is cited to show that in the case of a 50 per cent reduction when $d = 0.5\ D$ the compressive stress in the flange and the tensile stress over the radius are theoretically equal, yet the compressive stress must exceed the yield point of the metal before the drawing operation can really start and the tensile stress over the radius should not exceed the yield point by any great amount so that the shell wall will not be reduced in thickness. This places at 50 per cent the maximum reduction per operation even of metal which is sufficiently ductile to stand it.

There are, of course, some modifying considerations to this analysis as the metal in the flange strain hardens and S_c increases

from the yield point to the absolute ultimate strength at which all slip planes have been used up, a stress which is much higher than the nominal ultimate tensile strength. Accompanying this increasing unit stress, however, is the decreasing width of the flange which has a considerable compensating influence. The conditions are somewhat modified in certain cases by the use of relatively large punch and die radii which permit some stretching of the metal and start the flow gradually from the center rather than simultaneously across the whole flange. Cases which permit thinning of the shell wall beyond that which results from bending over the die radius, will sometimes show reductions in diameter in excess of 50 per cent, but these are relatively rare. Fig. 9 shows the recorded unit stress in the shell wall with reference to the elastic limit and nominal ultimate tensile strength for various per cent reduction in drawing a 3.75 inch diameter shell from 16 gage steel. It will be noticed that the greatest reduction, 46.5 per cent, resulted in shell breakage toward the end of the reduction due to the use of material (deep drawing steel) without sufficient ductility for so much plastic working. The stress in the side wall of this shell exceeds the nominal ultimate strength as obtained by the tensile test. The actual ultimate strength of this same material is believed to have been about 95,000 pounds per square inch, a stress which was probably developed in the flange area before failure.

Breakage Due to Strain Hardening

In arranging drawing operations, an aluminum manufacturer advises that he can perform three operations without annealing. Another manufacturer shows two severe redraws in steel, giving a total of 59 per cent reduction between anneals. A microscopic examination of the shell wall indicates that the material has been overstrained as internal fractures are apparent. A steel of higher carbon content might readily stand only half of this reduction before failing in a similar manner.

The amount of cold working which a metal will stand between anncals depends upon the rate at which it strain hardens. We have submitted data before the Institute of Metals, and in a more recent and considerably more extended discussion in the *Iron Age,* to show that, at a given temperature, a given metal will always strain harden at the same rate and to the same extent whether it is worked in tension or in compression. A means offered there for expressing per cent elongation, or per cent reduction in common terms, is a simple

logarithmic scale. Tentative rates of strain hardening for a few of the common metals are shown in Fig. 10. These are plotted against the actual unit stress resistance or unit strength of the metal on one coordinate and per cent reduction in section area, shell diameter, or sheet thickness on the other. The lower limit shown for each metal

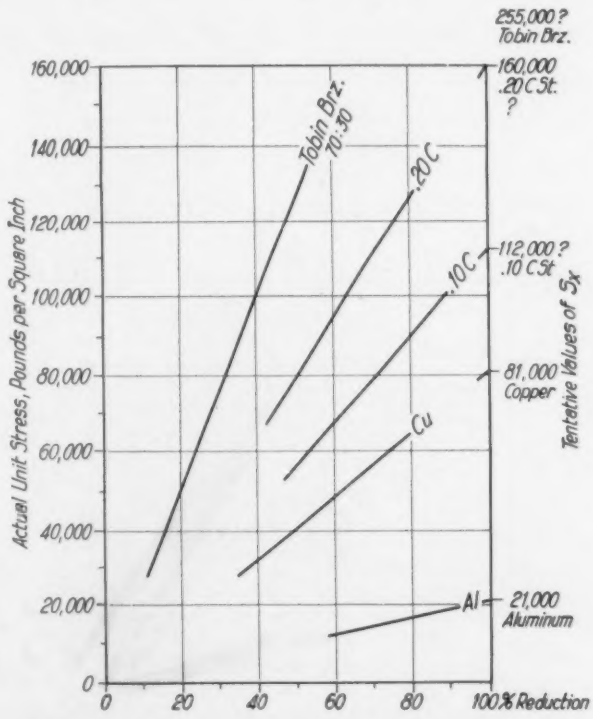


Fig. 10—Tentative Rate of Strain Hardening Curves at Room Temperature for Some of the Common Metals Showing the Plastic Range and Change of Stress.

is the commercially annealed state often designated as "soft" or "extra soft temper." Annealing might readily be continued further and further toward the single crystal state carrying the curves on down toward zero yield point at the origin. The upper limit in each case is the point at which all slip planes have been used up and internal fractures are likely to appear. The development of actual test curves will depart to a small extent from these curves both at the lower limit and the upper limit, but for theoretical purposes this may be neglected as it does not affect their practical use. The curves are continued to the point of their theoretical intersection with the 100 per cent absolute reduction line. This value, designated as $S_x/1.00$, may be used for reference as the rate of strain hardening at a given temperature.

Fig. 11 shows an example of the actual use of one of these curves, namely, the one shown for 0.10 per cent carbon steel. The shell, of about 14 gage, was blanked and drawn from S.A.E. 1010 extra deep drawing steel. This shell was then annealed and reduced in two draws by a total amount of 59 per cent. The two heavy

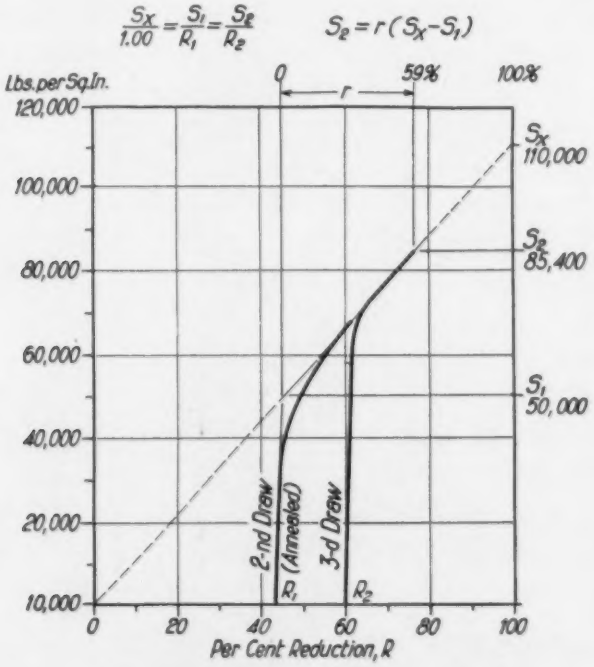


Fig. 11—To Illustrate the Use of the Tentative Strain Hardening Curve for S.A.E. 1010 Steel. Stress Curves are Drawn in for a Shell Commercially Reduced 59 Per Cent in One Anneal.

curves in Fig. 11 represent the compressive stress in the shell wall rising elastically to a theoretical yield point at the rate of strain hardening curve and then following that curve plastically to the point where the shell will be removed for the next draw. In the reduction, the stress rises elastically to the point reached at the end of the previous draw and continuous with the plastic movement along the rate of strain hardening curve to the completion of that reduction. There is a slight departure of the actual yield point from the theoretical yield point which is greatest in the annealed state. The resistance of the material rises during the 59 per cent reduction from 50,000 to about 85,000 pounds per square inch. It is interesting to note that specifications of this steel call for 55 per cent to 65 per cent reduction in the tensile test which brackets the 59 per cent reduction ob-

tained. A cross section of the shell well after the last reduction showed minute internal fractures indicating that all slip planes had been used up and a serious fracture was imminent.

The commonly given physical properties of metals are calculated to describe those metals in the state below the elastic limit for structural design purposes. Plastic working, however, involves a new set of properties entirely above the elastic limit. We have shown else-

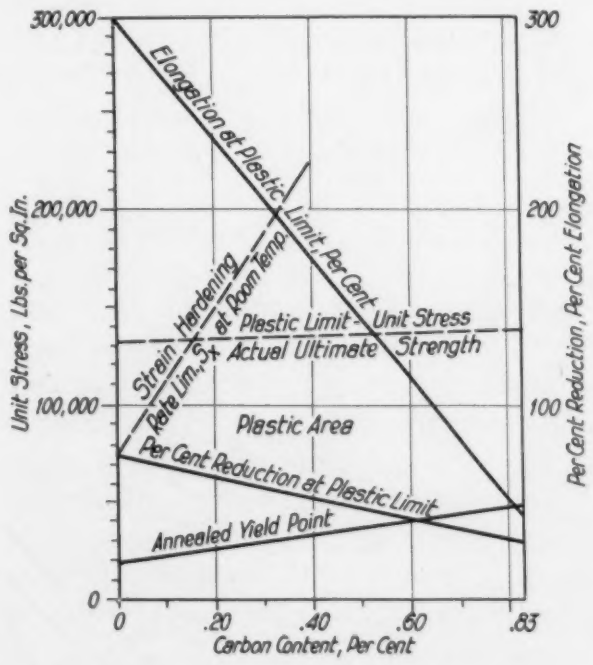


Fig. 12—A Tentative Illustration of the Change in Physical Properties of Carbon Steels Arranged with Reference to Plastic Working.

where experiments to demonstrate the progressively increasing yield point as metal is strain-hardened from the commercially annealed state to the plastic limit at which all slip planes have been used up. Fig. 12 is arranged to show the plastic physical properties of straight carbon steels according to their carbon content. The yield point in the annealed state is the lower limit of the plastic working range. Unit stress at the plastic limit is indicated tentatively in dotted lines. This is, for example, the true ultimate tensile strength or unit stress at the point where the fracture occurs. It is not a difficult value to get but our data at present are not sufficiently complete to give it with finality. The rate of strain-hardening increases rapidly as the carbon content increases. Our data on this curve for steels of different

carbon content are still too meager, however, to more than suggest its general direction. Fig. 12 also gives the per cent reduction in area which corresponds, of course, to the plastic limit and the ultimate elongation equivalent to this ultimate reduction. This, of course, is far higher than the nominal elongation in 2 inches which is not a true measure of what can be done in plastic working. The ultimate elongation at the plastic limit gives figures which at first seem extremely high. Examination of many drawing operations will show, however, that figures approaching the limits shown are actually obtained. In wire drawing, much higher figures have been recorded but here the working temperature is elevated considerably above room temperature with a resultant decrease in rate of strain hardening.

Annealing Troubles

In the course of their fabrication metals are frequently required to traverse the plastic cycle several times from the annealed state through plastic working to the strain-hardened state and back through recrystallization to the annealed state. Thus the cycle may be repeated two or three times in the process of cold rolling the strip or sheet. Subsequent reductions in preparing a drawn shell may require two or three more annealings. The formation of ears on drawn shells is attributed by competent investigators to directional properties resulting from unfortunate combinations of severe reductions and high temperature anneals.

Shell breakage is sometimes traceable to excessive grain growth around local areas with a resultant extreme local weakness compared with the rest of the shell wall. Germination or excessive grain growth is said to occur rather spontaneously in the lower carbon steels under favorable combinations of strain and annealing temperature. In any first operation drawn shell, the strain is evenly graded from practically nothing in the shell bottom through an increasing crystal distortion up the shell wall to a severely worked state at the top edge of the shell. This gradation of strain is likely to give an excessive grain growth at some level in the shell wall at almost any temperature providing sufficient time is allowed. One investigator has said that in the examination of many shells he has found some evidence of extra size grains at some point, usually the lower corner, in almost every case.

A thorough discussion of annealing should go also into the ques-

tion of pickling and cleaning, as these are of extreme importance to the drawn shell. Control of annealing times and temperatures should also be considered with reference to retaining a wall stiffness greater than the dead soft state while eliminating the working strain. This, of course, is a case of removing the shell as soon as recrystallization has taken place, but before there has been time for any grain growth. We wish, also, that there might be as clear a designation of tempers in rolled steel with reference to the strain hardening which has been undergone as is found in the brass and aluminum trades.

Die Construction

The principal details to be watched in die construction for drawing operations are the corner radii of the drawing die, the metal clearance, the shape of the drawing punch, finish of blankholding surfaces, and die material. Only very general rules can be given to cover most of these details as the shape of the piece, the metal used, the ultimate requirements, etc., often necessitate modifications. The edge of the die over which the metal is drawn is usually held to a radius of four to six times the metal thickness. Too sharp a radius results in excessive thinning of the metal and unduly high resistance to drawing over the edge. A greater radius may be used where the metal is sufficiently thick with reference to its diameter to preclude a chance of wrinkling. The shape used in single action drawing is often entirely different from that used for double action work as illustrated in Fig. 4. The straight bevel shown there is sometimes replaced with a parabolic curve starting with a relatively small radius at the top and increasing to a rather large radius at the throat of the die.

The clearance between the punch and the die is usually made considerably more than the metal thickness to permit thickening up and easy flow over the edges. If ironing is required, however, the clearance may be held down to the original metal thickness or less. In normal free drawing operations where the thickening up is not objectionable, the clearance may be as high as 50 per cent more than the metal thickness for the first operation draw and 25 per cent more than the metal thickness for redrawing operations.

The nose of the drawing punch should also have a radius of four to six times the metal thickness in order not to cause thinning of the metal as it is bent over the edge of this punch. The radius, of course, may be increased to a very much greater amount providing that the

metal is not so thin compared with its diameter as to cause the formation of wrinkles as has already been discussed. In certain classes of operations where the shell is to go through several reductions, a taper of perhaps 45 degrees may be used on the nose of the drawing punch, and a similar taper used on the blankholding surface of the next redrawing operations. Here again the corner should not be too sharp as it would thin the metal and cause a local weakness.

It is usually essential to have a very carefully finished surface, particularly on the blankholding surface and over the drawing edge, in order to avoid picking up the material and also breakage when the draw is very severe. In shallow drawing operations or draws which involve very large unbalanced stresses as at the corners of rectangular shapes, it may occasionally prove necessary to actually arrange the blankholding surface to retard the flow of the metal. This is usually done by the insertion of draw beads; that is to say, a groove may be furnished in the die surface parallel to the drawing edge and a corresponding bead placed on the blankholding surface so that metal flowing into the die must flow over the draw bead.

The metal used for the drawing die is of particular importance to life of the tools in points of wear and picking-up, or welding. If long wear is not vital, and picking-up should be avoided, cast iron die rings are reasonably satisfactory and hard aluminum bronze rings are very much better. A chromium-nickel cast iron mixture is also used with considerable success. Where cast die rings are relatively thin, they are quite easily broken by accidental double blanks and should be supported in a holder of sufficient strength or reinforced with a shrunk ring around it. In this case, a taper ring is usually used to back up the drawing ring securely in the holder. If production is very large, it is usually necessary to use hardened steel dies, especially the alloy steels with considerable chromium content. Chromium plating of steel dies for drawing operations has also been employed with considerable success in many places.

The reason for picking up may possibly be that from time to time a crystal in the metal being drawn becomes aligned with a crystal of identical orientation and lattice on the die surface under such conditions of pressure and temperature that inter-atomic attraction between the two crystals will be greater than the boundary forces of the crystal in the drawn sheet so that it will tear out and remain attached to the die. Once this process is started, the metal builds up on the welded particle quite easily. For that reason, the use of metals which

are more or less dissimilar, as in the case of machine bearings, should reduce, and does seem to reduce, the tendency to pick up. Increased speed, of course, results in increased heating, which favors the welding process. It may be noted in this connection that brass can be drawn on steel at speeds up to 200 feet per minute, whereas steel on steel can only be drawn at 50 or 60 feet a minute. Possibly steel could be drawn much faster over the hard aluminum bronze dies.

DISCUSSION

Written Discussion: By Felix F. Aloi, Seneca Iron and Steel Co., Buffalo, N. Y.

The author is to be congratulated on this excellent paper which helps to bring the art of plastic drawing nearer to a science. This paper has given us a clearer understanding of that vague property of sheet steel usually termed "flowing quality."

It has often been said that the successful plastic drawing of sheet steel into shapes depends on three factors, steel sheets of good drawing quality, proper die construction and an intelligent press-room operation. The author has clearly brought out that none of these factors can be overlooked.

The question of what properties are necessary in a sheet, to place it in the extra deep drawing range, has been answered by the author, that is, the rate of plastic hardening, which depends on the grain size, is the important factor. The sheet manufacturer uses two things to control grain size, chemical analysis and heat treatment.

If two pieces of sheet steel, say 20 gage, are placed in an Erichsen sheet tester and a cup is drawn into the two pieces, the cup formed will be deeper than when only one piece is used. How does the author account for the increase in the depth of the cup when using two pieces, and could this idea be used commercially to form deeper stampings?

Written Discussion: By Alfonso E. Lavergne, mechanical engineer, Edward G. Budd Manufacutring Co., Philadelphia.

I have read Mr. Crane's paper with a great deal of profit. I was especially interested in the data he gives regarding the tentative strain-hardening rates. The conclusion is reached by Mr. Crane that a given metal strain-hardens at a definite rate from the beginning of the cold working regardless of the rate of deformation. I do not believe this to be so. From some preliminary experiments which we have conducted with low carbon strip steel (0.037 inch thick) we found that when the tensile specimens were pulled at rates which varied from ¾ inch per minute to 240 inches per minute very different results were obtained. In the particular steel with which I worked, when the rate of deformation increased to 19 inches per minute, premature fracture occurred. By premature fracture is meant that fracture took place before parts of the specimen had been plastically strained. It would seem to me, therefore, that the rate of strain-hardening is also dependent upon the rate of deformation.

Referring to Mr. Crane's paragraph on page 172, in which he says, "The percentage reduction in area which corresponds, of course, to the plastic limit and the ultimate elongation equivalent to this ultimate reduction; this, of course, is far higher than the nominal elongation in 2 inches, which is not a true measure of what can be done in plastic working."

I should like to say that it is very difficult to determine the reduction in area of specimens of rectangular cross section, namely, 0.750 inch wide by, say, from 0.030 to 0.090 inch in thickness. Average reduction in area throughout the entire specimen could easily be obtained with the aid of a planimeter, but there is a question in my mind as to the utility of such average results.

Curiously enough in dealing with rectangular specimens one finds that by slight variations in heat treatment, yet within the same chemical analysis (0.005 to 0.012 per cent carbon), the same reduction in area may be obtained in two specimens, but such percentage reduction in area would be in one case brought about by a drastic reduction in width, while in the other by a drastic reduction in thickness.

It should be noted that in such cases, although the percentage reduction in area is the same in both specimens, these two materials would behave quite differently in deep drawing.

It seems to me that the per cent elongation in 2 inches, although it may not be a strictly accurate measure of maximum plasticity, gives an indication of the possibilities of the material. The percentage elongation in a larger gage length would obviously give an indication of the uniformity of extension throughout the test specimen, which for certain stampings is also important.

Written Discussion: By R. L. Kenyon, supervising research engineer, American Rolling Mill Co., Middletown, Ohio.

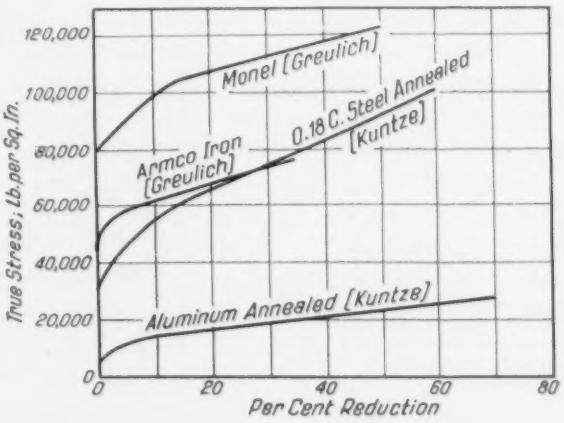
The many variables which enter into the deep drawing operation have discouraged many engineers from attempting a rigid mathematical analysis of the various relationships which exist. Mr. Crane is to be complimented on this excellent paper which presents a great deal of useful information on this important problem. There are a few points, however, on which the writer is not in full agreement with the author and others on which further information would be helpful.

In the discussion of buckling on the sixth page, the impression is gained that irregular patches of coarse grains are one frequent cause of this trouble. Sheets of good drawing quality are quite uniform in grain size, but will buckle under certain conditions of loose hold-down, etc. Would it not be better to assign the buckling merely to eccentric loading in compression? This may be due to slight lack of flatness of the original blank or flange when it occurs on a subsequent draw, or it might result from lack of flatness of the hold-down itself. It is known from experience that a stiff sheet is more apt to buckle than a soft one.

In continuing this discussion the author states that draws can be made without a hold-down and not suffer wrinkling if the "metal is so thick relative to the average grain size that nonuniformities in the distribution of large and small grains, or of grains of varying crystal orientation, are averaged

out so that the stresses are practically uniform." Here again it is believed that grain size and grain uniformity are of secondary importance, at least in sheets of good deep drawing quality. It is probable that the significant relationship is between blank thickness and diameter of punch.

The roughening of the surface sometimes observed over corners or other places of excessive local stretching, is due to coarse grains. It is true that this is due to slip plane movements, as the author has indicated, but the important point is that this slip phenomenon which occurs alike in fine and coarse-grained material is not detected when the grains are fine, because of



the minuteness of the individual grains. The net effect in such material is a fine matted surface which is only slightly "dulled" in the case of very small grains. The roughness is a direct function of grain size.

The demonstration on the thirteenth page of the maximum reduction per operation is, of course, only approximate. The author mentions the modifying considerations of friction and the extra force required for bending over the radius. He also states that the material in the flange is hardened by cold working, thus increasing S_c. No mention is made of the increase in tensile strength of the material in the side walls. This metal is being cold-worked also and simultaneously strengthened. The net result is that variations in unit strength and in cross section are taking place continuously in both flange and side wall and it would seem that any attempt to determine analytically the limiting reduction per operation must take into consideration all of these modifying conditions. Knowing the rate of strain hardening and the change in section, it should be possible to apply the proper corrections for S_c and S_t.

The curves shown in Fig. 10 are all straight lines which pass through the origin. This does not agree with similar data given in the literature. The curve shown above combines the results of two investigators.

The stress increases rapidly up to the yield point with practically no reduction in cross section. The point where the curve intersects the stress axis should, therefore, correspond to the yield stress.

The author also states that single grained material should have a zero yield point. The reason for this statement is not apparent, as a definite force would be required to produce the slip planes of even a single crystal.

On the seventeenth page reference is made to a specification of 55 to 65 per cent reduction of area for 14 gage extra deep drawing steel. This is the first case that has come to our attention in which reduction of area has been specified on sheet material. It is a very difficult quantity to measure on this material and it would be interesting to know if this is being done to any considerable extent.

The quantities plotted are of considerable theoretical interest, but the author does not indicate their application to the drawing problem. For example, it is not shown that the "elongation at plastic limit," which is also termed relative elongation, has any bearing on deep drawing. This is usually determined by computing what extension a tensile sample would have shown if all of the gage length had suffered the same reduction in cross section as that at the fracture. In deep drawing we are interested in the amount of elongation that occurs before local reduction takes place rather than the theoretical amount that would occur under a set of conditions that do not occur in practice.

In making these comments on Mr. Crane's paper, it is not the writer's intention to detract in any way from his valuable contribution to the literature on this subject. There is a great deal to be done in both experiment and theory before the problems of deep drawing will be completely understood. This paper is an excellent starting point for those who wish to study this subject.

Author's Closure

In reply to Mr. Aloi it is the writer's opinion that the cupping test is almost wholly stretching and does not simulate drawing operations. It might be that, in cupping two sheets together, the flange area is not gripped as tightly as with one sheet, or that a difference in relation of blank diameter to thickness would favor the ease of flow and permit a deeper cup, but that is conjecture.

There would not seem to be any real advantage to commercial drawing in using more than one blank at a time, except to increase production where the shells may be easily separated and size is not essential. Taper-sided foil bottle caps are frequently carried through a number of draws in pack form before separation. If spinning operations are employed to finish a shell to size and remove wrinkles, it is possible to draw taper or conical shells in a pack of two or more. Two sheets may also be drawn together where it is desired to produce a straight shell of one metal lined with another metal. There is no resultant bond between the two except friction.

In reply to Mr. Lavergne may I say that there is one property of metals which varies greatly with speed of test and that is per cent of elongation. Time is apparently essential in the selection of the weakest area for local failure. Jeffries and Archer (The Science of Metals) quote tests showing elongation in 2 inches for a given steel, varying from 27 per cent at the speed of a testing machine, to 47 per cent under a drop hammer, and 62 per cent due to a gun powder explosion. All, of course, are far below the ultimate elongation occurring locally at the neck. The same authors note that "the force required to deform a single crystal is practically independent of

any time effect," which, we believe, is applicable to the cold working of most metals in press operations.

The comment that test elongation in 2 inches is not a true measure of what can be done in plastic working is meant to point out that a steel showing 42 per cent elongation in 2 inches may readily be drawn in one operation (say 40 per cent reduction), enough to elongate a unit area in the side wall by 66 per cent. The ultimate elongation of the same steel would be about 185 per cent at fracture.

We appreciate the difficulty in measuring per cent reduction in area on strip specimens and the confusing effect of directional properties.

We appreciate Mr. Kenyon's very thorough discussion and will follow it through in order.

Regarding buckling and the formation of wrinkles, we do not believe that methods of grinding and finishing the blank-holding surfaces of the tools would permit sufficient irregularity to account for wrinkle formation. Other discussion at the Boston meeting pointed out distinct nonuniformity through the thickness of drawing sheets even with notable differences in composition near the surfaces. We do not feel that any great difference in crystal size is essential to cause wrinkles to start in relatively thin material when it is not positively held flat. It would be natural that "stiff sheet is more apt to buckle than soft," as the stiffness is due to strain hardening in rolling and is likely not to be uniform through the thickness of the metal. Such strain hardening also increases the resistance of the metal to the plastic work in drawing and, therefore, increases the stresses which would tend to form wrinkles.

We agree with Mr. Kenyon that the significant relationship in the matter of wrinkle formation is between blank thickness and punch diameter, but still feel that the fundamental reason for the significance of that relationship must be traced back to the relation of grain sizes to thickness and to each other.

Mr. Kenyon is quite correct in bringing out the fact that differences in surface roughening or dulling are "a direct function of grain size."

The tensile strength of the metal in the side wall of a shell does increase due to strain hardening, but varies from zero increase at the bottom corner or punch radius to a maximum at the top of the first operation shell (or part way up on subsequent reductions). Most shell failures occur partly for this reason and partly due to reduction in thickness by bending at a point near the bottom corner radius, so that the increase in tensile strength at points higher up would seem to be of relatively little practical use.

The series of photographs reproduced by Mr. Kenyon agree in type with the curves used by the writer as a starting point in obtaining the curves shown in Fig. 10. The reason for transposing these curves to a common origin, however, was to make them mathematically comparable and to eliminate the wide variation in their yield point, due to annealing practice or to cold working after annealing. This and the question of attributing zero yield point to the single crystal state have been discussed at greater length by the writer in a recent series of articles in *Iron Age* and more briefly in a paper on metal working in power presses presented before the American Institute of Mining and Metallurgical Engineers.

We appreciate that it is rather difficult to measure reduction in area of sheet material. We must admit that our work to date has been largely in theory and experiment. We must disagree, however, with Mr. Kenyon on the relative values of general elongation at the point where necking usually starts in the tensile test and ultimate strength elongation and reduction at the point where failure actually occurs at the neck, which we believe is approximately the plastic limit. The low general extension before necking of the tensile test and the cupping test has been shown to be subject to wide variation with speed of test and is also a very much lower value than the actual increase in length of unit areas found in the walls of many drawn shells. The ultimate values, both of reduction and elongation, as found at the neck, are real limits, however, and are approached but not exceeded in drawing operations. We have offered examples to illustrate this in Fig. 11 and in the more complete *Iron Age* series.

LUBRICANTS USED IN DEEP DRAWING OF SHEET STEEL

By Maurice Reswick

Abstract

This paper makes an analysis of the nature of the stresses involved in deep drawing practice, in so far as they pertain to lubrication, and emphasis is laid on the fact that the subject of lubrication has not received the attention which it deserves, largely through the lack of co-operation between the metal fabricator and the lubricant manufacturer. The required characteristics of an ideal lubricant for deep drawing are set forth to be as follows: film strength, oiliness, adhesiveness and spreading, ease of cleansing, noncorrosiveness, stability and uniformity, physiological effect, no disagreeable odor, little variation with climatic changes, and low cost. A description of the principal ingredients which enter into the manufacture of drawing compounds, together with reasons why certain characteristics are imparted by them to the lubricant is discussed. Reference is also made to the latest developments in the field of lubrication, especially to "border-line" lubricants, which may be applied to drawing compounds in perfecting a lubricant that will prevent metal-to-metal contact between the work-piece and the dies. The paper is concluded with the listing of the analyses of five typical drawing compounds which were found to be successful in actual practice. Throughout this paper, the author has endeavored to present the subject from the user's standpoint, to which the chemists and lubricant manufacturers must adapt themselves.

Introduction

CONSIDERABLE progress has been made in recent years in deep drawing practice of sheet steel, and the art has been extended in many directions, with drawn sheet steel shapes replacing castings, sections built up by riveting or welding, and intricate parts forged under the hammer. The fundamental process involved in

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, Maurice Reswick, is Chief Engineer, Pennsylvania Lubricating Co., Pittsburgh. Manuscript received July 8, 1931.

the stamping and drawing of metals at ordinary temperatures is that of plastically working the metal in compression or squeezing, and in tension or elongation, subjecting it to local stresses beyond the yield point without exceeding its ultimate strength.

In the formation of cupped shapes, depending on the relative stresses involved, the degree of working may be classed as ordinary stamping, shallow drawing, deep drawing, extra deep drawing, and extra-extra deep drawing, referring to each step or press operation. The term "deep drawing", therefore, does not depend on the comparative size of the work piece, but on the ratio of the principal dimension of the piece before drawing to the corresponding dimension after the drawing operation.

In this paper, the operations usually understood as "deep drawing" will be considered, in which the plastic stresses approach the ultimate strength of the sheet steel, so that any deductions arrived at may be readily applied to the less severe cases.

Lubrication a Neglected Subject

As in the case of engineering and machinery construction in general, the subject of lubrication in metal drawing is still regarded as being of secondary consideration to the design of machinery and dies and to the improvement in production methods. In fact, the attitude of some operators is to regard lubrication as a necessary evil instead of a useful function in the conservation of dies and tools and as a means of improving the quality and quantity of output. Until recently each fabricator of metal developed his own lubricants by the expensive "cut and try" and "hit or miss" method, without a comprehensive understanding of the basic requirements.

The literature of the stamping and drawing trade is abundant with engineering information and operating data, but there is an obvious scarcity of published articles on the vital subject of lubrication. This is due in equal measure to the failure of the metal fabricator to appreciate the scientific phase of this subject and to the reluctance of the lubricant manufacturers to disclose what they consider as trade secrets, gained at considerable expense in their research laboratories and in field experiments. As the development of an efficient lubricant depends on the science of chemistry and the art of compounding as much as it does on a knowledge of the operating problems involved in the drawing of sheet steel, it is obvious that the

problem of lubrication can be best solved by mutual effort and by entrusting its solution to the technical staff of lubricant manufacturers who make a specialty of developing special lubricants for particular jobs, and who are in a position to utilize their experience in related problems of lubrication.

Scope and Object

This paper discusses in general terms the fundamental requirements of an ideal lubricant for deep drawing operations, in the hope that it may serve as a starting point for a more complete symposium at a later date. As far as possible, the subject will be treated from the user's standpoint, whose requirements are definite and clear cut, and to which the lubrication chemist must adapt himself.

Required Characteristics

The primary function of a lubricant for deep drawing operations is to prevent metal-to-metal contact between the work-piece and the dies, and also to decrease the sliding friction to a minimum. The degree to which a lubricant comes up to these requirements is a measure of its efficiency and value.

The most satisfactory procedure in purchasing a lubricant for any purpose, whether for general bearing lubrication or for specific application to deep drawing, is not on the basis of analytical specifications nor on prescribed laboratory tests, but on the basis of satisfactory performance on the job. Accordingly, an ideal lubricant which meets the requirements of deep drawing operations, must possess the following characteristics in the order of their importance:

1. Film Strength. The lubricating film or coating must be strong enough to withstand the enormous pressure prevailing within the plastic range of the worked material under compression, so as to prevent metal-to-metal contact both under static and "flow" conditions of the worked metal. Scoring and abrasion of the dies and work-piece must be prevented, as well as "pick-ups" of the softer metal on the hardened die surface. It is generally agreed that where two rubbing surfaces are of the same metal, without an interposing lubricating film, scoring and "pick-ups" are the result of actual fusion of the microscopic surfaces in direct contact, due to the intense localized heat generated from friction, even though the duration of the phenomenon is only momentary. Aside from the heat due to

rubbing friction of the metallic surfaces, there is also generation of heat due to the plastic deformation of the metal worked, and it is essential that the lubricating film must not be unduly thinned down and weakened at the higher temperature.

2. *Oiliness.* The coefficient of friction between the die surface and work-piece must be low, so that a minimum amount of energy be expended in "skin" friction, both in the forward or working stroke and in the backward or pull-back movement of the dies. Lack of oiliness in the lubricant used results in localized drawing, or in uneven elongation and wall thickness. When working on steel sheets of light gage, especially in flanging operations, fracture of the metal and development of seams and cracks should be reduced to a minimum when a good lubricant is used.

3. *Adhesiveness and Spreading.* The lubricant must adhere to the surface of the metal without being unduly tacky. It must also spread itself under the pressure of the dies in such a way that it will form a protecting film ahead of the working portion of the die. It should also be sufficiently light in body and possess marked affinity for the metallic surface so that it may be applied manually by means of a brush or mechanically by means of an automatic spraying device or through plastic gelatine-like rolls.

4. *Ease of Cleaning.* As the finished product from the draw press or stamping machine must generally undergo a further process of plating, tinning, galvanizing, lacquering, or painting, it is essential that all traces of the lubricant used must be easily removed by means of readily obtainable and cheap cleanser, such as simple mixture of caustic soda. This requirement is generally met in a drawing compound that emulsifies in water.

5. *Noncorrosiveness.* The lubricant must not contain mineral acids of any kind that may attack the worked metal, should the cleansing process be delayed for any reason. Nor should there be any tendency to pit the surface of expensive dies and machinery used.

6. *Stability and Uniformity.* The drawing compound must be stable in composition, and there must be no separation into its component parts during storage and handling, nor should it become rancid, decomposed or otherwise spoiled. One shipment must be exactly the same as the previous shipment, unless some modification was made in the formula by mutual agreement to meet a special working condition. This requirement is largely a problem of the lubricant manufacturer.

7. Physiological Effect. The lubricant must be absolutely neutral in its physiological effect on the machine operators, and must not contain any ingredients which may lead to poisoning through skin absorption or inhalation of fumes, nor shall it produce such skin diseases as pimples, eruptions, or boils. As a further precaution, it might be permissible to introduce into the lubricant a harmless antiseptic like creosol.

8. Odor. No perceptible disagreeable odor should be noticed. The addition of a perfuming substance to disguise the real odor of the lubricant should be avoided.

9. Effect of Climatic Conditions. There should be no pronounced change of the consistency or other properties of the lubricant with the usual variations of temperature and humidity between summer and winter weather.

10. Economy. The drawing compound must be low in cost. With some metal fabricators this item is of first consideration, but logically, the relative cost of the lubricant should be regarded not on the basis of its price per pound or per gallon, but on the basis of its cost per thousand pieces finished, considering also the quality of the product and the wear on the dies and tools. An appreciable saving may be effected by purchasing a lubricant not only of the best quality for the purpose, but also in the most economical form. For example, a certain manufacturer in the middle west was able to reduce his lubrication cost by more than 50 per cent through the simple expedient of purchasing only the "base" of a soluble compound and by mixing it with water at his factory to the proper consistency. His reasonable claim that the waters of Lake Erie are not any worse than the waters of the Delaware River, cannot be denied, and there is certainly no justification for him to pay freight charges across several states on an abundant commodity like water. This, of course, is an extreme case, but illustrates the point.

A drawing compound that would meet the above ten requirements 100 per cent is the ideal to which the grease and oil manufacturers are striving, and which the users are hoping to get sometime before the millennium. Unfortunately, in the art of lubricant manufacture, especially in the making of compounded lubricants like grease and drawing compounds, a particular characteristic in the finished product is most usually obtained only at the sacrifice of another, often equally important, property of the lubricant. Hence, the best drawing compound that is possible to produce consists of a

compromise, with every point gained being at the expense of another point. The expertness and skill exercised in the compounding of a lubricant that would possess the greatest degree of advantage and efficiency is what differentiates one lubricant manufacturer from another.

Specific Purpose Drawing Compounds

While a so-called "general purpose" drawing compound may be prepared that will answer about 75 per cent of deep drawing operations in a more or less satisfactory way, it is realized that working conditions vary to a great extent, and out-of-the-ordinary situations are of frequent occurrence. The complexity of the workpiece, design of dies, wall thickness, speed of operation, kind of metal or alloy used, surface characteristics, physical properties, evenness of anneal, etc., are all factors which must be considered. The drawing of low carbon steel, higher carbon steel alloys, stainless steel, brass, aluminum, etc., all require different methods of handling, and for a first-class job the type of lubricant used must also be modified accordingly, or "tailored" to the particular job.

For light work, whether in ordinary stamping or in deep drawing, a simple compond of a soluble oil is all that is necessary, while for heavier classes of work, special lubricants are required. Some of the lubricants used in drawing steel are decidedly unsuitable for drawing aluminum, for which the drawing compound must be free from alkalis which combine with aluminum forming aluminum salts. In the absence of a better lubricant, on some work powdered copper, or even sheets of paper are used to secure separation of the die from the work during the drawing operation. These simple expedients are better than no lubrication at all, but it is advisable to replace them with more efficient lubricants which are now on the market, and which were developed in the research laboratories of lubricant manufacturers and have received adequate tests in the field to prove and establish their merits.

Composition of Drawing Compounds

The principal ingredients entering into the compounding of lubricants for deep drawing will now be enumerated and an effort will be made to state their functions, giving the reason *why* they impart certain characteristics to the lubricant.

1. *Tallow.* This is the oldest and still most extensively used ingredient in the compounding of all kinds of greases and drawing compounds. Tallow, in its raw state, is a lubricant of the first order, but its inherent properties are brought out to best advantage when it is combined in the form of soap with certain metals such as calcium, sodium, potassium, lead, aluminum and zinc. The addition of tallow or other animal fats to any lubricant enhances its "oiliness," increases its film strength, and makes it adhere to the metallic surface better. In press work, it is claimed that tallow follows ahead of the die, creating a lubricating film on the surface of the workpiece before the die penetrates or comes in contact with fresh surfaces. The use of tallow in the raw state is inconvenient and objectionable because of its tendency to become rancid and wormy. It is difficult to apply it to large work, while modern conditions of speed and pressures demand that its inherent properties of oiliness and other desirable characteristics be still further enhanced by the admixture of other substances. From the point of economy, tallow and other animal fats and oils in raw state, like lard oil, are more costly than compounded lubricants.

In the same class with tallow, other fats and fixed oils like lard, palm oil, etc. may be mentioned. The best drawing compounds contain the best grade of these fats, especially those having a high melting point, or a high titer value.

2. *Mineral Oil.* Nearly every lubrication job requires the use of mineral oil in one form or another. In general, the greater the viscosity of the oil, the stronger is the film strength and the greater is the adhesion to metallic surfaces. In a drawing compound, the objectionable feature of using too large a percentage of mineral oil is the difficulty in cleaning the product with simple mixtures like caustic soda, unless special cleaning compounds like benzine, naptha, and other solvents are used. Hence, in a first class drawing compound the percentage of mineral oil must not be excessive, and should be preferably in combined form with other ingredients like soda base soap and other emulsifying substances.

3. *Water.* Water is present in a lubricant as an emulsifier, in which case it serves the function of acting as a binder between the animal oils, mineral oils, soaps, and other ingredients. A definite percentage of water in emulsified form is necessary, but any excess of it may be regarded as a diluent controlling the consistency of the drawing compound.

From the standpoint of cleansing requirements, it becomes necessary to combine the mineral oils, animal or vegetable oils, and all other ingredients, in such manner that the resulting drawing compound will be of a soluble nature, or in the form of a colloidal emulsion. This is usually accomplished by the introduction of a soap, like soda or potassium soap, which dissolves in water.

4. *Fillers.* In a grease used for the lubrication of general machinery, the presence of filler materials like chalk, soapstone, mica, rosin, graphite, fireclay, potters clay, borax, etc., is regarded as being objectionable, and all standard specifications outlaw these adulterants. In drawing compounds, however, where the relative speed of the rubbing parts is extremely slow, and the coefficient of friction is not necessarily required to be at a minimum, the presence of fillers is not only permissible, but even desirable. These fillers, while they coarsen and cheapen the grease, serve the useful function of increasing the strength of the lubricating film by the simple expedient of thickening the film, so that a greater pressure acting over a longer interval of time will be required to rupture the film. These fillers are also somewhat unctuous in their nature, or "slippery" to touch, but they do not possess any pronounced lubricating properties. While in regular machine lubrication practice they would be considered as being of a decided abrasive character, in drawing work they may be considered as passable and allowable. Fillers, like mica and graphite in particular, perform the further function of acting in a limited degree as solid lubricants, the claim being made that even when the mineral or fatty lubricating film is broken down, the graphite or mica still acts as the medium of preventing metal to metal contact. These fillers should be used, when necessary, in a highly pulverized form, so that their abrasive action be reduced to a minimum. In addition to "thickening" up the lubricating film, fillers also serve the purpose of filling up the unevenness of the metallic surfaces on the work piece, so that when the smooth, hardened dies come in contact with it, the possibility of scratching the die and causing pick-ups is reduced.

Certain fillers, like soapstone and chalk, may be present in combined form with the other ingredients of the drawing compound, and even when they are in a free state, they are not particularly objectionable when it comes to the cleaning operation because they can be completely washed away with the caustic soda cleaning fluid. Such fillers, however, like graphite, which is a chemically inert substance,

cannot be washed away readily, especially since minute particles of graphite are likely to become embedded or anchored into the microscopic pores of the metal. Hence, in general, the use of graphite and mica in drawing compounds should be limited to very low quantities, and when the drawn or pressed product is to undergo further operations of electro-plating, fillers of this type must not be used at all.

"Border-Line" Compounds

Within recent years startling progress was made in the field of general lubrication by the development of oils and greases containing lead oleate, and experiments are at present in progress to apply this ingredient to drawing compounds. Lead oleate compounds are

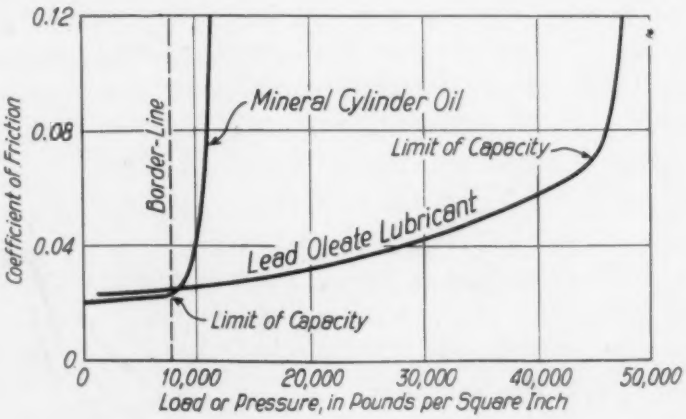


Fig. 1—Comparison of Lead Oleate and Mineral Oil.

known as "border-line" lubricants, and may be best defined graphically by referring to Fig. 1, which is based on actual tests, using a straight mineral oil and a lead oleate compound, both having the same viscosity. A good lubricating film was maintained with the mineral cylinder oil until the load reached 7000 pounds per square inch, at which point the coefficient of friction began to rise rapidly, so that between 7000 and 10,000 pounds per square inch load the film was practically all squeezed out. The "border-line" is, therefore, here indicated at 7000 pounds per square inch of load. To the left of the "border-line" there was perfect fluid friction; to the right of the "border-line" lubrication was only partial at first, resulting in semi-solid friction, while at the 10,000 pounds load there was nearly solid friction. Hence, with straight mineral oil it is not safe to exceed a unit pressure of 7000 pounds per square inch. In case of the lead

oleate compound, while the coefficient of friction was slightly higher from the start, effective lubrication was maintained until a pressure of 45,000 pounds per square inch was reached, which marks its limit of capacity, before the state of semi-solid friction was approached. In other words, the protection obtained with the lead oleate compound, as shown in this test, was more than six times greater than with a mineral cylinder oil of the same viscosity.

Analyses of Drawing Compounds

Several analyses of typical drawing compounds on the market are given. These are not formulas which may be used in the manufacture of a drawing compound, but are merely laboratory analyses of actual samples which may be made by any analytical chemist. As stated previously, the analysis of a drawing compound gives only an approximate idea of what the various constituents are, but it fails to reveal the more essential information as to how the various ingredients are combined. Two chemists using the same formula will produce two products which are different from each other in stability, lubricating properties, and even in appearance—as too many factors are involved in the actual manufacture, such as temperature control, the order in which the ingredients are mixed to prevent internal chemical interaction, and the skill required in making successful emulsions and colloidal suspensions.

Analysis of Drawing Compounds

	No. 1	No. 2	No. 3	No. 4	No. 5
Unsaponifiable Matter	20.90[1]	.....	.....	49.00[4]	.....
Unsaponifiable Neutral Fat	7.60	50.22[2]	.....	.....	.....
Free Fatty Acid	6.70	12.41	.....	3.00	.....
Sodium Soap	23.80	.....	54.00[3]	.....	.....
Water	41.00	31.51	46.00	30.00	32.00
Potassium Soap	.....	5.86	.....	18.00	.....
Lime Soap	.....	.....	.....	.....	6.00
Mineral Oil	.....	.....	.....	.....	22.00[5]
Mineral Filler	.....	.....	.....	.....	40.00
Total	100.00	100.00	100.00	100.00	100.00

[1]Unsaponifiable matter used was a mixture of cylinder oil and petrolatum. The fatty material was a mixture of palm oil and tallow.

[2]The fatty material used was a low grade tallow of rather poor odor.

[3]The fatty material used in the soap was a mixture of vegetable oil and animal fat.

[4]Unsaponifiable matter was a 300 viscosity at 100 degrees Fahr. engine oil. The fatty material was Elaine Oil.

[5]Mineral oil used was a pale product with a viscosity of 190 at 100 degrees Fahr. Fatty material used in the soaps was an animal fat of low melting point. The mineral filler present was of the colloidal clay type.

ACKNOWLEDGMENTS

The author wishes to take this occasion to express his indebtedness to H. F. Lefurgy, chemist, Pennsylvania Lubricating Co., who has furnished the analyses of the drawing compounds given above together with other chemical data. Also to C. B. Karns, manager Pittsburgh Works, Standard Oil Co. of Pennsylvania, for assistance and helpful criticism in the preparation of this paper.

DISCUSSION

Written Discussion: By H. T. Morton, metallurgist, Hoover Steel Ball Company, Ann Arbor, Mich.

In this paper, Mr. Reswick has brought out the essential requirements of lubricants for deep drawing. Each of his ten factors must be considered in selecting the best lubricant for each application. However, three factors contribute to cause the deep drawing dies to "pick-up" metal. These are: characteristics of the deep drawing steel; hardness of the dies; and the lubricant.

Grain growth on the surface of the steel or steel with a very low Rockwell hardness value will "load-up" the dies more readily than harder steel with a uniform grain structure.

When the dies are soft the metal tends to drag over the surface instead of slide. Thus several sets of high carbon high chromium steel dies with a Rockwell hardness of 56-58, C scale, had to be polished after every 9000 parts had been formed. These dies were re-hardened to a Rockwell hardness of C 63-64 and used on the same steel with the same lubricant, giving runs in excess of 40,000 parts before repolishing.

Thirdly, the lubricant is of importance but will vary in composition according to specific requirements. For light work as mentioned by Mr. Reswick an ordinary soluble oil containing lard oil and sulphur or similar constituents is satisfactory. For heavy material or extra deep drawn parts the lubricant should contain tallow, lard oil, or palm oil, either as a fat or as a soap and may contain a filler. Personal tests indicate a preference for graphite added to the fat containing mineral oil on severely drawn parts.

Written Discussion: By E. V. Crane, staff engineer, E. W. Bliss Company, Brooklyn, New York.

Regarding "picking-up" in drawing operations, Mr. Reswick suggested in his paper that sufficient heat may be generated in drawing to cause actual fusing of the metal to the die. We know that considerable heat is generated but do not believe that it approaches remotely near the fusion temperatures. We have the suggestion, however, that in the case of similar metals, as in drawing steel over steel dies, a sufficiently intimate junction may be obtained between the metal being drawn and the metal in the die so that crystals in each, which will occasionally happen to be oriented in the same way, will have between them a force of atomic attraction sufficient to pull out the crystal in the sheet being drawn and attach it to the crystal of similar orientation and

space lattice on the surface of the die itself. Once that action is started, the building up of additional metal by erosion will obviously follow. We would appreciate comments on this situation.

Oral Discussion: By H. F. Lefurgy, chief chemist, Pennsylvania Lubricating Company, Pittsburgh.

I would say that the use of graphite or filler in any deep drawing lubricant is to be avoided, if possible, for the simple reason that it is very hard to keep in suspension. For that reason when we manufacture deep drawing lubricants we have tried to find some other medium, and in our research we have turned to the lead oleate product. We find that when lead oleate is added in different proportions to different kinds of mineral oils, we have a product that will replace those lubricants which contain tallow and graphite and a great many fillers, and to date we have used it with a great deal of satisfaction and success. The only difficulty we find at present with the lead oleate products is that they are not soluble in water and therefore they cannot be cut back and it is very difficult to wash them off.

However, certain users are very pleased with these products because they overcome a great many difficulties that have been encountered with the other type of products containing fillers and water soluble soaps. They usually dip the metal in hot water and then wipe it. It takes a little longer but there are less rejections. The deep drawing lubricant is the hardest product we have to make from the standpoint of obtaining a homogeneous mixture. With ordinary tube drawing lubricant we can make a product which is readily soluble in water and has a great deal of slip, but when we come to the deep drawing lubricant we have to give it a certain amount of adhesiveness and that is brought about only by loss of water solubility, and when you get into the fillers, as I briefly stated, it is very hard to keep them in suspension and usually when the manufacturer buys them, he may have to keep them stirred.

Author's Closure

Mr. Crane's reference to the theory of orientation of crystals and atomic attraction as an explanation of the phenomenon of "pick-ups" on dies, certainly appears to be as valid and logical as the author's attempt to account for it by the generation of localized heat on microscopic areas which leads to direct fusion. An idea of the effect of intense localized heat may be gained by observing the manner in which an ordinary match is ignited. The coating on the tip of the match (particularly the so-called "safety matches") does not become ignited unless it is brought in contact with a very hot substance, but when the match is rubbed against a prepared rough surface the heat localized at the microscopic rubbing areas is sufficiently high to ignite the match tip.

In all probability "pick-ups" are the result of accidental orientation of the crystals of the metals in contact, the action being accelerated under localized heat conditions. In any event, it is common knowledge that "pick-ups" whatever their cause may be, can be prevented by the interposition of an effective lubricating film between the surfaces of the die and the worked metal.

SOME MOLYBDENUM HIGH SPEED STEELS

By Joseph V. Emmons

Abstract

An investigation has been made of the properties and performance of several types of molybdenum high speed steels. The mechanical properties of hardness, strength and plasticity have been determined for each type of steel through an extensive range of heat treatments.

The microstructures have been studied and interesting observations discussed.

The cutting quality has been determined by means of an extensive series of drilling tests. Brief correlations are made between the cutting quality, the structure and the mechanical properties.

Comparisons are made between the molybdenum steels and some well known types of tungsten high speed steels.

A new type of molybdenum high speed steel, carrying about one-fourth as much tungsten as molybdenum, has been developed and found to be superior in many respects to the molybdenum high speed steels previously examined.

MOLYBDENUM high speed steels have been known almost as long as those made with tungsten. They were investigated extensively by Messrs. Taylor and White (1),* as well as by many others. Important recent developments have been reported from the metallurgical laboratory of the Watertown Arsenal by Captain Ritchie (2). An historical account of these early experiments is given in the monograph, "The Alloys of Iron and Molybdenum," (3) recently prepared for the Alloys of Iron Committee at the Battelle Memorial Institute. This monograph contains such a complete bibliography that only a few special references to the literature seem necessary here.

It has been the general opinion of previous investigators that the role of molybdenum in high speed steel is as a replacement element

*The numerals enclosed in parentheses pertain to the references appended to this paper.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, Joseph V. Emmons, a member of the society, is metallurgist, Cleveland Twist Drill Co., Cleveland, Ohio. Manuscript received July 1, 1932.

for tungsten. It has been the intent in the investigations here reported to consider molybdenum in high speed steels not as a substitute but as an alloy with an individuality of its own. It has been hoped that some information would thus be gained to assist in determining the potential field of molybdenum high speed steels in industry.

The method of attack has been by means of an investigation of the mechanical properties of hardness, strength and plasticity, in a manner which has been previously described (4), (5). These mechanical properties have also been supplemented by a study of the microstructure and a determination of the cutting quality of the steel by means of drilling tests. The method used in determining the cutting quality of a steel by means of drilling tests may be described as follows:

Drills are usually made in two sizes, such as ¼ inch and 1 inch in diameter. From three to twelve drills are tested of each size, the larger number being used when it is desired to determine the best of several promising heat treatments. Each drill is given three or four tests in different materials, the point being reground for each test. All tests were run to a finish, that is, until the drill will no longer cut. The materials drilled are such as S.A.E. 1040, having a Brinell hardness of about 170; S.A.E. 3335 heat treated to a Brinell hardness of about 225; chromium die steel annealed to a Brinell hardness of about 210, and hard cast iron having a Brinell hardness of about 200. The standard of comparison is the performance of drills of the 18-4-1[1] type of steel which are included in each test. In order to obtain a numerical basis for comparison, the results of each test are calculated as a percentage with the performance of the 18-4-1 drills taken as 100 per cent. The percentages earned by the drills of a certain steel in each material are then averaged together to form a final performance percentage. These final performance percentages thus represent an average of from ten to twenty individual tests of different sizes of drills in a wide variety of materials and under different operating conditions. When several heat treatments which differ widely have been tried, the one producing the best results is used for the average. It is believed that such an average performance rating is much more valuable than the results of any single test, no matter how conducted.

[1]18.00 per cent tungsten, 4.00 per cent chromium, 1.00 per cent vanadium.

At the initiation of the experiments here reported there were no molybdenum high speed steels available on the market. This may be taken as an indication that the general consensus of opinion in the tool steel industry was, that molybdenum high speed steels were not able to compete successfully with those made from tungsten. Such samples of experimental steels as remained in the hands of the previous experimenters questioned, were found to be either insufficient in quantity or unsuitable in form for the desired determinations of the mechanical properties. It was found necessary in order to obtain the amount of steel required in suitable form to have experimental heats made up to our own specifications. At first the compositions of these experimental heats were planned according to the theories advanced by various previous investigators. Later, as sufficient information accumulated, new types of compositions were tried along the lines which appeared most interesting.

The first experiments were made upon molybdenum high speed steels of the type of composition shown in Table I. In these steels the molybdenum is intended to completely replace the tungsten. Different investigators have reported various ratios in which they believed molybdenum should be used to replace tungsten in high speed steel In general these ratios have been for one part of molybdenum to replace from two to three parts of tungsten. Steels made in accordance with some of these ratios have been arranged for comparison in order of the ratio in which the molybdenum replaced the tungsten referring to the 18-4-1 type of high speed steel as a standard. It is believed that the steels in this table represent good ex-

Table I
Molybdenum High Speed Steels, Tungsten-Free

Steels	Carbon	Chromium	Tungsten	Vanadium	Molybdenum	Ratio(a)	Tungsten Equivalent(b)
I	0.69	3.38	None	1.37	6.49	2.9	12.98
II	0.62	3.90	0.17(c)	1.03	6.74	2.7	13.65
III	0.71	2.66	None	0.79	6.87	2.6	13.74
IV	0.57	3.48	None	0.87	7.39	2.4	14.78
V	0.66	3.70	None	1.19	8.26	2.2	16.52
VI	0.76	3.77	None	1.21	9.03	2.0	18.06
VII	0.66	4.26	0.10(c)	1.14	10.19	1.8	20.48
VIII	0.82	3.55	None	1.01	10.72	1.7	21.44
IX	0.69	3.66	None	1.01	14.46	1.2	28.92

(a) The product of this ratio and the molybdenum content is equivalent to approximately 18 per cent tungsten.

(b) This tungsten equivalent is based upon the common assumption that one per cent of molybdenum is equivalent to two per cent of tungsten.

(c) These traces of tungsten are accidental.

amples of the various types of compositions proposed by previous investigators.

As Steel IV may be regarded as typical of this group, the study of its properties will be reported in some detail. A series of hardening and tempering temperatures was selected to cover the range expected to be useful. In the schedule which follows, each "X" represents a heat treatment given to a set of two specimens:

Hardening Schedule

Hardening Temperature	Tempering Temperatures									
	Not Tempered	440°F (225°C)	540°F (280°C)	640°F (340°C)	740°F (395°C)	840°F (450°C)	940°F (505°C)	1040°F (560°C)	1140°F (615°C)	1240°F (670°C)
2090°F (1140°C)	X		X	X	X	X	X	X	X	X
2130°F (1165°C)	X		X	X	X	X	X	X	X	X
2165°F (1185°C)	X		X	X	X	X	X	X	X	X
2200°F (1205°C)	X	X	X	X	X	X	X	X	X	X
2235°F (1225°C)	X		X	X	X	X	X	X	X	X
2270°F (1240°C)	X	X	X	X	X	X	X	X	X	X

The response of the steel to these heat treatments is shown by the curves in Figs. 1 to 2. The results obtained upon the duplicate specimens were averaged to obtain the value plotted. From a study of these curves it is observed that there are many points of similarity to the curves for the 18-4-1 tungsten high speed steel previously shown (5). For convenience of comparison these curves for the 18-4-1 type of steel are here repeated as Figs. 3 and 4.

There is a material difference in the response of the two types of steel to variations in hardening temperatures, the most favorable hardening range being much lower for the molybdenum steel than for the tungsten. The maximum secondary hardness[2] observed in the molybdenum steel is developed at a hardening temperature of 2270 degrees Fahr. (1240 degrees Cent.), which is about 130 degrees Fahr. (55 degrees Cent.) lower than for the 18-4-1 steel. The maxi-

[2]The terms secondary hardness and secondary strength refer to the hardness and strength as developed by a high tempering temperature in the vicinity of 1000 degrees Fahr. (540 degrees Cent.).

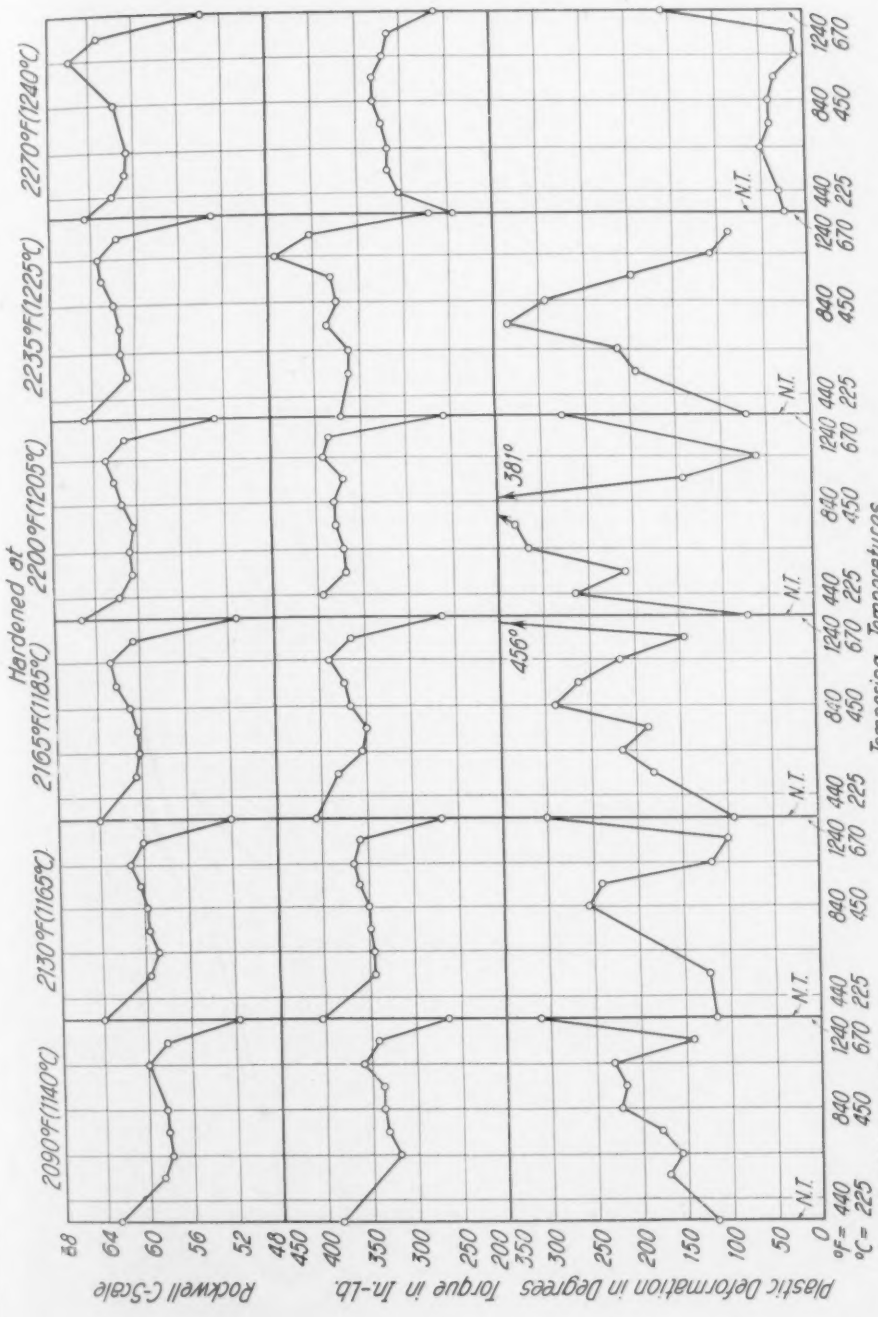


Fig. 1—Steel IV. (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

mum secondary strength[2] observed was developed at a hardening temperature of 2235 degrees Fahr. (1225 degrees Cent.), which is about 115 degrees Fahr. (45 degrees Cent.) lower than for the 18-4-1 steel. Other points upon which the molybdenum steel was observed to differ from 18-4-1 are:

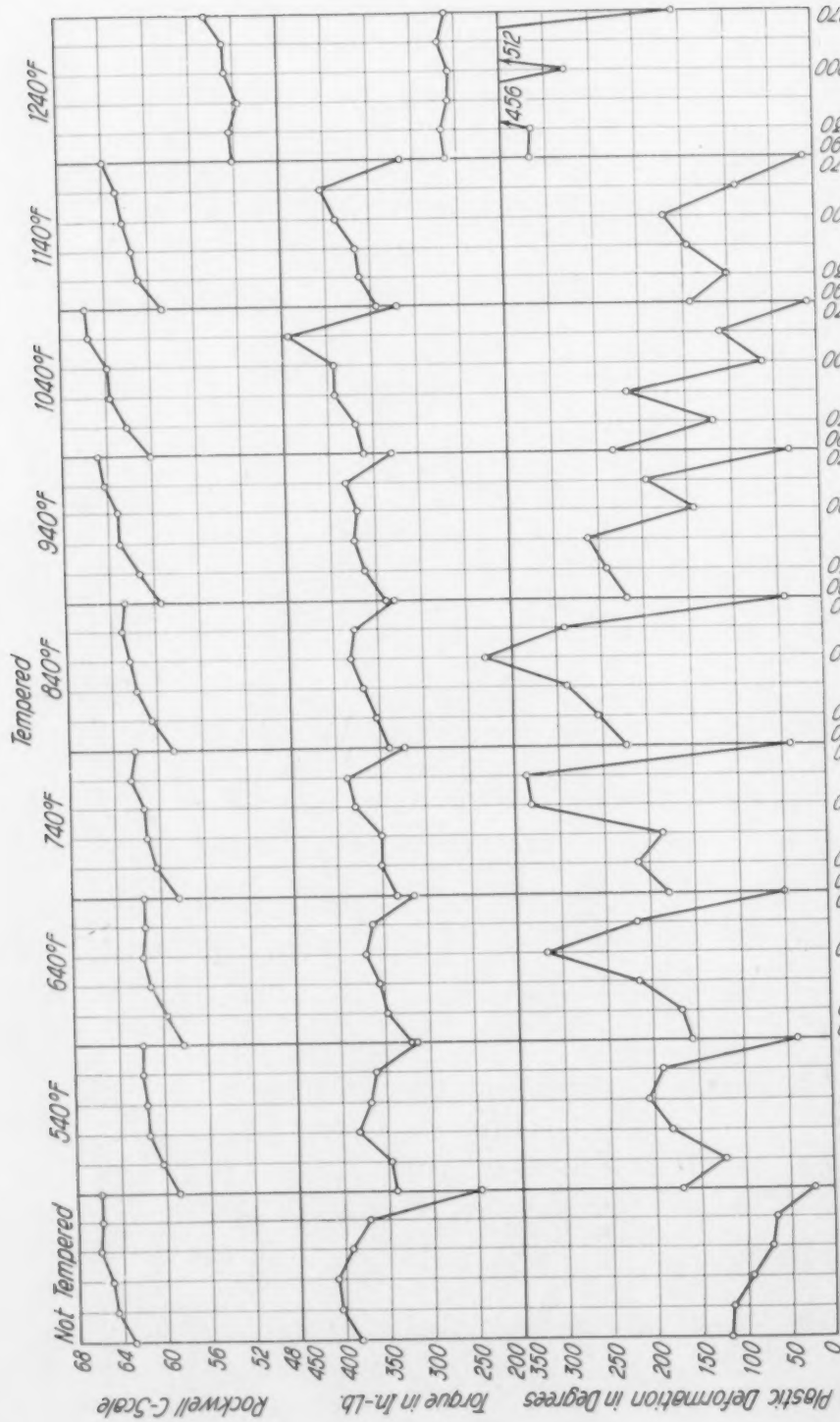


Fig. 2—Steel IV. (Upper Set of Curves) Rockwell Hardness versus Hardening Temperatures; (Middle Set of Curves) Ultimate Torque versus Hardening Temperatures; (Lower Set of Curves) Plastic Deformation versus Hardening Temperatures.

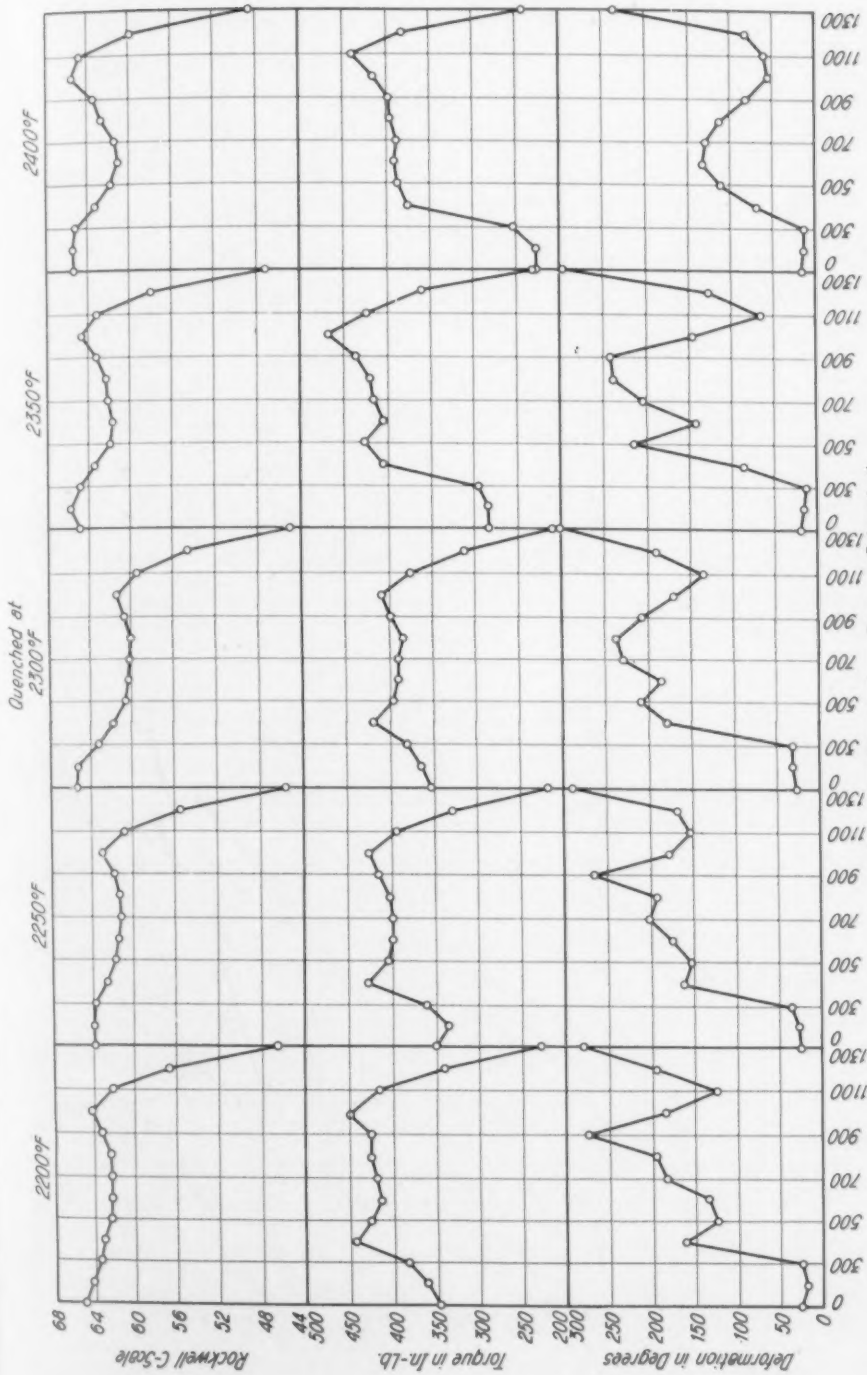


Fig. 3—Steel XXII (18-4-1), (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

The hardnesses are generally not as high for the lower hardening temperatures, although the maximum secondary hardness is slightly higher.

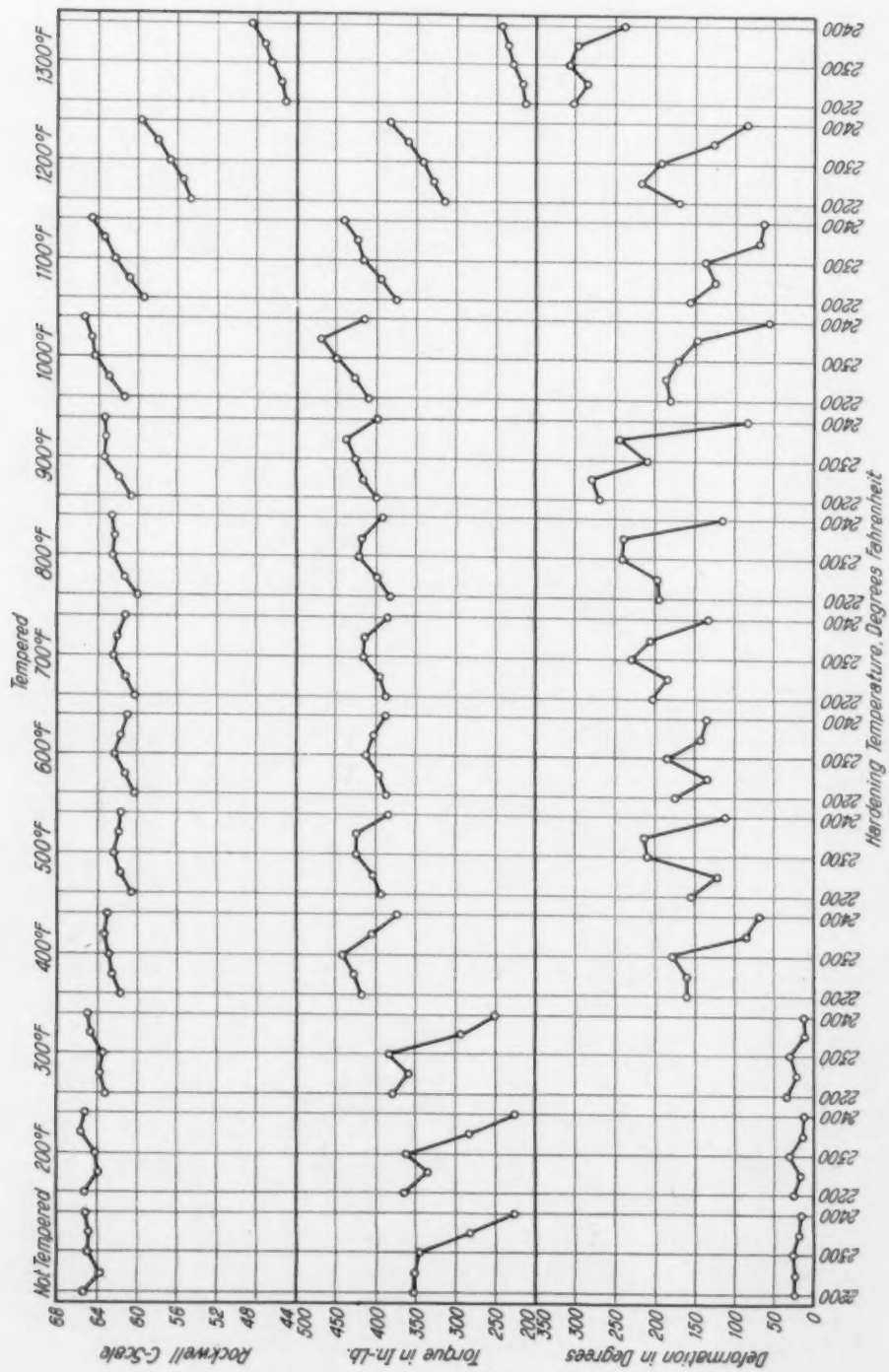


Fig. 4—Steel XXII (18-4-1), (Upper Set of Curves) Rockwell Hardness versus Hardening Temperatures; (Middle Set of Curves) Ultimate Torque versus Hardening Temperatures; (Lower Set of Curves) Plastic Deformation versus Hardening Temperatures.

The strength of the molybdenum steel is generally higher than that of the tungsten steel before tempering and lower thereafter.

The range of hardening temperatures in which a high secondary

strength is maintained appears to be narrower in the molybdenum steel.

The plastic deformation shows wider fluctuations than with the 18-4-1. It attains high values before tempering and at the intermediate tempering temperatures, but shows a more abrupt falling off at high hardening temperatures.

Limitations of space will not permit the inclusion of complete curves for all the steels in Table I. Some of the most interesting data are shown in Table IV. General comparisons are made as follows:

Steel No. 1 having higher carbon and vanadium contents and lower molybdenum shows a very similar range of properties. The maximum strength is developed at a hardening temperature of 2200 degrees Fahr. (1205 degrees Cent.), which is 35 degrees Fahr. (20 degrees Cent.) below the corresponding temperature for Steel IV. The plastic deformation is generally lower and decreases rapidly at hardening temperatures above 2200 degrees Fahr. (1205 degrees Cent.).

Steel II having slightly higher carbon, chromium and vanadium contents, together with a trace of tungsten, shows similar mechanical properties to Steel IV.

Steel III having a higher carbon and a lower chromium content develops its maximum secondary hardness at a hardening temperature as low as 2200 degrees Fahr. (1205 degrees Cent.), which is 70 degrees Fahr. (40 degrees Cent.) below the corresponding temperature for Steel IV, and 200 degrees Fahr. (110 degrees Cent.) below this temperature for the 18-4-1 type of steel. This maximum of secondary hardness is also maintained over a wider range of both hardening and tempering temperatures, than is the case with Steel IV. The maximum secondary strength is developed at 2165 degrees Fahr. (1185 degrees Cent.), which is 70 degrees Fahr. (40 degrees Cent.) below the corresponding temperature for Steel IV. The maximum plasticity develops at a tempering temperature of 640 degrees Fahr. (340 degrees Cent.), which is much lower than with Steel IV.

Steels V and VI did not have sufficient material available to permit a determination of the mechanical properties.

Steel VII having higher carbon, chromium, vanadium and molybdenum contents, shows hardness curves surprisingly similar to those of Steel IV. The maximum secondary strength is less than

Fig. 4—Steel XXII (18-4-1). (Upper Set of Curves) Rockwell Hardness versus Hardening Temperatures; (Middle Set of Curves) Ultimate Torque versus Hardening Temperatures; (Lower Set of Curves) Plastic Deformation versus Hardening Temperatures.

Hardening Temperature, Degrees Fahrenheit

for Steel IV, and tends to develop at a tempering temperature about 20 degrees Fahr. (10 degrees Cent.) lower. The plasticity at all heat treatments is much lower than for Steel IV.

Steel VIII with higher carbon and molybdenum contents also shows hardness curves quite similar to those of Steel IV. The strength curves show a higher average than observed in Steel IV. The maximum secondary strength is the highest observed for any of the steels in Table I. It is the only tungsten-free steel showing a secondary strength which approaches that of the 18-4-1 Steel XXII. The plastic values are upon a lower level than those of Steel IV, although the shape of the curves is generally similar.

Steel IX having a higher carbon content and a much higher molybdenum shows a radical change in the curves for all of the physical properties. The hardness and strength have fallen off to values which are below the range of usefulness for cutting tools. The plasticity has moderate values but has become unresponsive to variations in heat treatment.

Microstructure of the Tungsten-Free Steels in Table I

Photomicrographs are shown of some typical structures of a few of these steels. Particular attention is called to the fine structure of the martensitic matrix, which in some cases appears to have an important influence upon the results obtained from the steel.

Fig. 5 shows Steel IV at its maximum observed strength. The structure is quite similar to that of the 18-4-1 steel in Fig. 11, except that the carbide masses are fewer and smaller.

Fig. 6 shows Steel IV at its maximum observed hardness. The austenitic grains are quite large. The carbides are few, small and are concentrated principally on the grain boundaries. They are beginning to show a cubical shape.

Fig. 7 shows Steel I at its maximum observed strength. The structure is similar to that of Steel IV in Fig. 5. The increase in carbon content has not been sufficient to produce a considerable increase in the number of carbides.

Fig. 8 shows Steel III at its maximum observed strength. The martensitic structure is sharper and cleaner cut than in Fig. 5. While the carbon of this steel is up to 0.71 per cent, the structure contains relatively few carbides. The austenitic network has been almost completely obliterated by the high tempering temperatures.

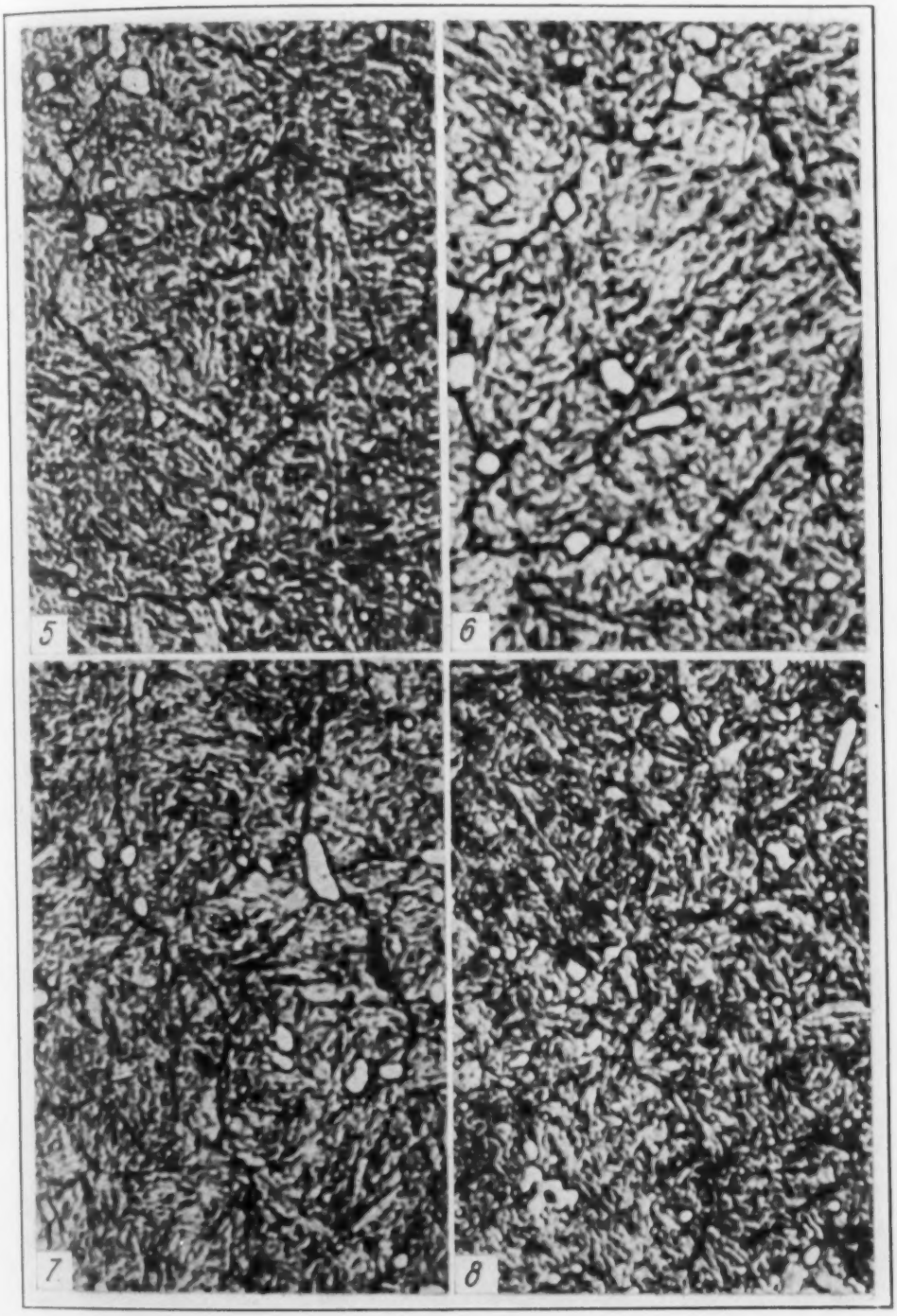


Fig. 5—Steel IV, Structure at the Maximum Strength Hardened at 2235 Degrees Fahr. (1205 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

Fig. 6—Steel IV, Structure at the Maximum Secondary Hardness, Hardened at 2270 Degrees Fahr. (1240 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

Fig. 7—Steel I, Structure at the Maximum Strength, Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

Fig. 8—Steel III, Structure at the Maximum Strength, Hardened at 2165 Degrees Fahr. (1185 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

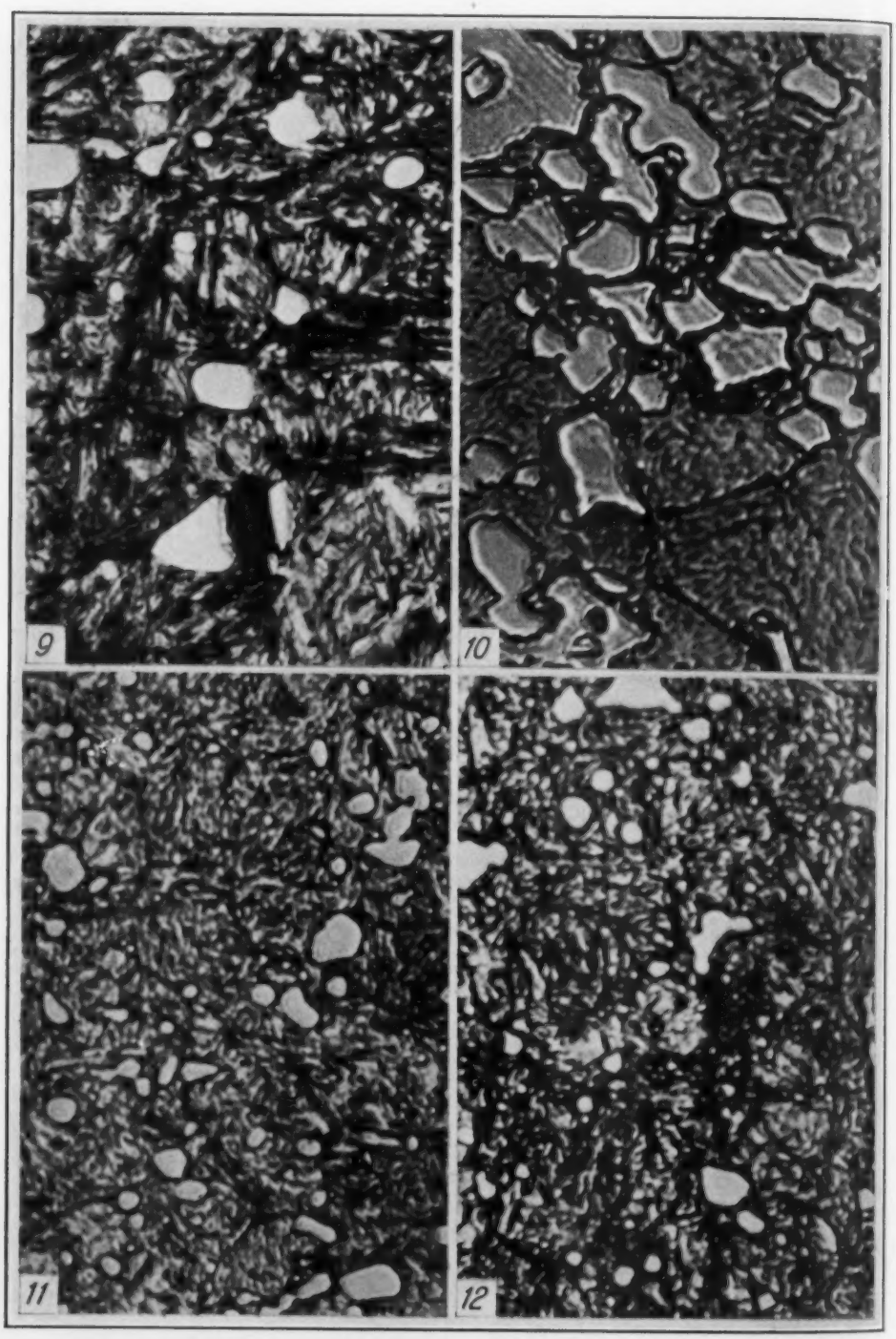


Fig. 9—Steel VIII, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 2000.

Fig. 10—Steel IX, Structure at the Maximum Strength, Hardened at 2270 Degrees Fahr. (1240 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 2000.

Fig. 11—Steel XXII (18-4-1), Structure at the Maximum Strength, Hardened at 2360 Degrees Fahr. (1290 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

Fig. 12—Steel XVII, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 1800.

Fig. 9 shows Steel VIII at its maximum observed strength. This structure varies widely from that in Figs. 5 and 11. No austenitic grains are visible. The martensitic structure is coarse and shows many straight clean cut needles with but few of the distorted or vermiform variety. The carbides are present in considerable quantity and are gathered into large masses.

Fig. 10 shows Steel IX at its maximum observed strength, which was quite low. This is an entirely different structure from that normally observed in high speed steel. Traces of austenitic grain boundaries are still visible. Some martensite is present in a fine vermiform structure. Carbide masses are present in considerable numbers and in large sizes. A soft constituent resembling ferrite now occupies about twenty per cent of the area. The masses of this soft constituent are frequently bounded by dark troostitic borders which merge gradually with the martensitic areas. This structure is interpreted to indicate that the very large amount of molybdenum in this steel has combined with so much of the available carbon to form carbide that there is not enough carbon left in solution to form a complete martensitic structure.

Fig. 11 shows a typical structure of an 18-4-1 steel at its maximum observed strength. It is included for the purpose of comparison.

Performance Data

The performance ratings or the determinations of the cutting quality by the method previously described are summarized in the last column of Table IV. It will be observed that the performance ratings do not parallel the variations of any of the mechanical properties there tabulated. Neither does the performance of a steel bear any simple relation to its molybdenum content as shown in Table I. The poorest performance was recorded for Steel III, in which the chromium was conspicuously low. The best performance was recorded for Steel VIII, in which both molybdenum and carbon were high. It is definitely shown by the results upon Steel IX that increasing the molybdenum content much above 11 per cent in a steel of this general composition will seriously lower both the hardness and the strength to the point where cutting quality will be low.

It seems definitely established that the performance of this type of steel is materially below that of the 18-4-1 type as illustrated by Steel XXII. As a type it is more nearly on a par in cutting quality

with the 15-4-1 type of high speed Steel XXI. A number of attempts have been made to improve the cutting quality of these molybdenum high speed steels. Steels IX, XVII, XVIII and XIX were made for this purpose.

It has already been shown by the results on Steel IX that increasing the percentage of molybdenum beyond a certain point will produce diminishing returns.

Steels XVII and XVIII are attempts to improve the properties of two varieties of molybdenum steels by the addition of cobalt. By reference to Table VI, it will be seen that the addition of cobalt has produced steels with high strength and hardness but with low plasticity and cutting quality. The structure of Steel XVII at its peak of strength is shown in Fig. 12. Faint traces of austenitic grains are visible. The martensitic structure is fine and distorted. The carbides are normal in size and quantity and show even distribution.

Steel XIX was made to determine if an addition of nickel would improve the properties of the tungsten-free molybdenum steels. The summarized data in Table VI show that while the hardness has been maintained, the strength and the performance have both been lowered. The plasticity was not materially changed. The tempering temperature at which the maximum secondary strength is developed was raised from 1040 to 1140 degrees Fahr. (560 to 615 degrees Cent.).

An Attempt to Improve Molybdenum High Speed Steels By Relatively Small Additions of Tungsten

It was concluded in some of the early experimental work with the straight molybdenum high speed steels, that the necessity of using low hardening temperatures to secure adequate grain refinement and strength was a disadvantage which perhaps partially explained the low cutting quality observed. The coarse martensitic needle shapes which were developed by the hardening temperatures producing the peaks of strength were also believed to be detrimental to the cutting quality. Among the other attempts made to raise this permissible hardening temperature, to refine the martensitic structure and to improve upon the cutting quality, the addition of a moderate amount of tungsten was tried. Encouraging results led to the investigation of a series of steels of this type. Table II shows the compositions of six such steels covering a considerable range of variations in composition.

Steel XII has been selected as being representative of the type. The response of its mechanical properties to variations in heat treatment will be shown in detail. In the following schedule of heat treatments each "X" represents a heat treatment given to a set of two specimens from this steel.

	Tempering Temperatures									
Hardening Temperatures	Not Tempered	440°F (225°C)	540°F (280°C)	640°F (340°C)	740°F (395°C)	840°F (450°C)	940°F (505°C)	1040°F (540°C)	1140°F (615°C)	1240°F (670°C)
2130°F (1165°C)	X	X	X	X	X	X	X	X	X	
2165°F (1185°C)	X	X	X	X	X	X	X	X	X	
2200°F (1205°C)	X	X	X	X	X	X	X	X	X	X
2235°F (1225°C)	X	X	X	X	X	X	X	X	X	X
2270°F (1240°C)	X	X	X	X	X	X	X	X	X	X
2310°F (1265°C)	X	X	X	X	X	X	X	X	X	X

The data upon the mechanical properties of these specimens are shown plotted in the form of curves in Figs. 13 and 14. In these curves the duplicate specimens have been averaged to obtain the value plotted. Particular attention is called to a few of the relations between these curves and the corresponding ones for Steels IV and XXII. The hardness curves are similar to those of Steels IV and XXII.

The strength curves have been powerfully affected by the tungsten addition. The strength of Steel XII before tempering is much lower than for Steel IV, and more nearly like that of Steel XXII. With increasing tempering temperatures the strength of Steel XII increases rapidly so that the average strength after tempering is higher than that of Steel IV. Steel XII develops maxima of strength when hardened at both 2200 degrees Fahr. (1205 degrees Cent.) and 2235 degrees Fahr. (1225 degrees Cent.), and tempered at 1040 degrees Fahr. (560 degrees Cent.) which are not only superior to the highest strength observed for Steel IV, but are also equivalent to the highest observed strength for Steel XXII (18-4-1). At a hardening temperature above the one at which the maximum strength is

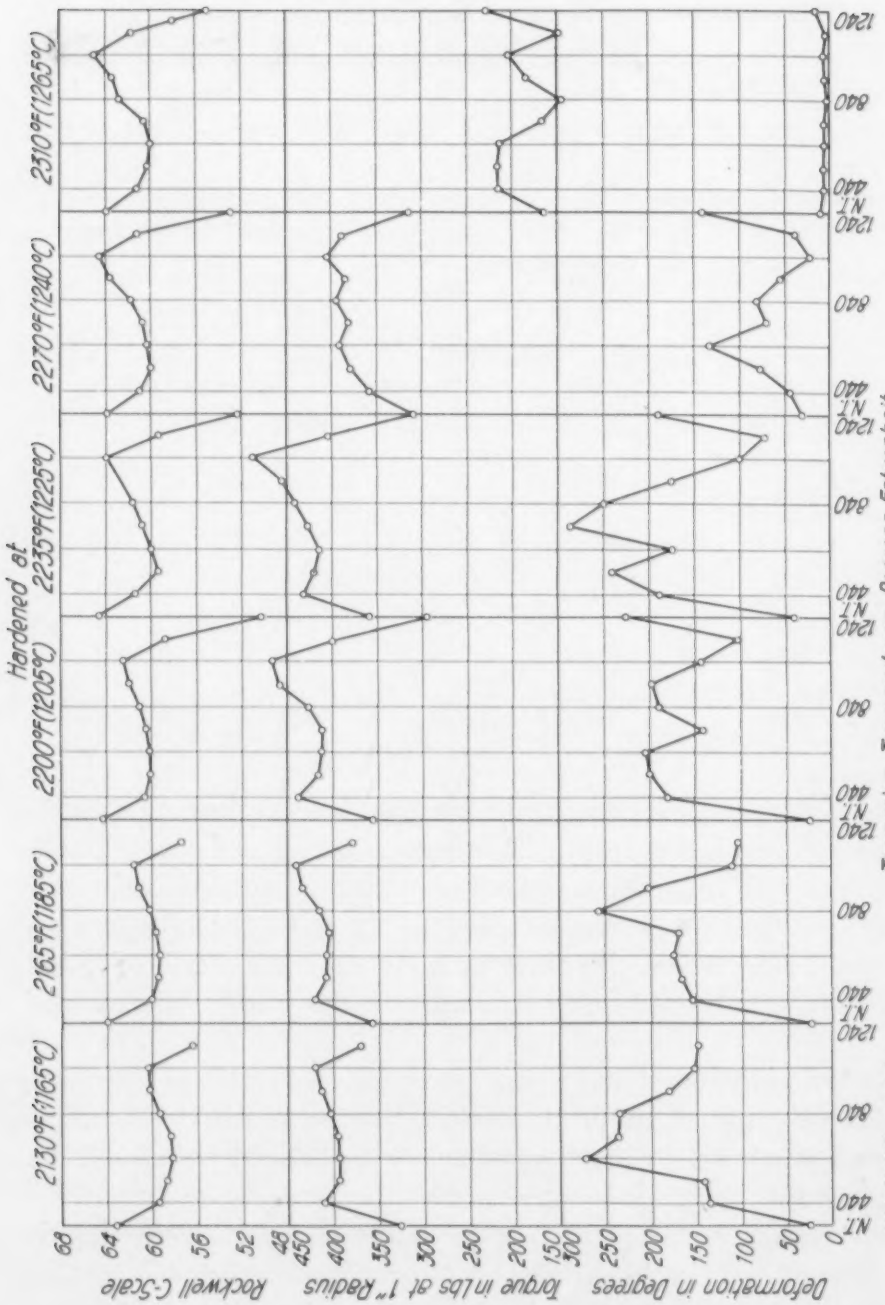


Fig. 13—Steel XII. (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

developed the strength of Steel XII appears to fall off less rapidly than Steel IV, but more rapidly than Steel XXII. In general the strength curves more nearly resemble those of Steel XXII than those of Steel IV.

The plasticity curves for Steel XII do not show the wide fluctua-

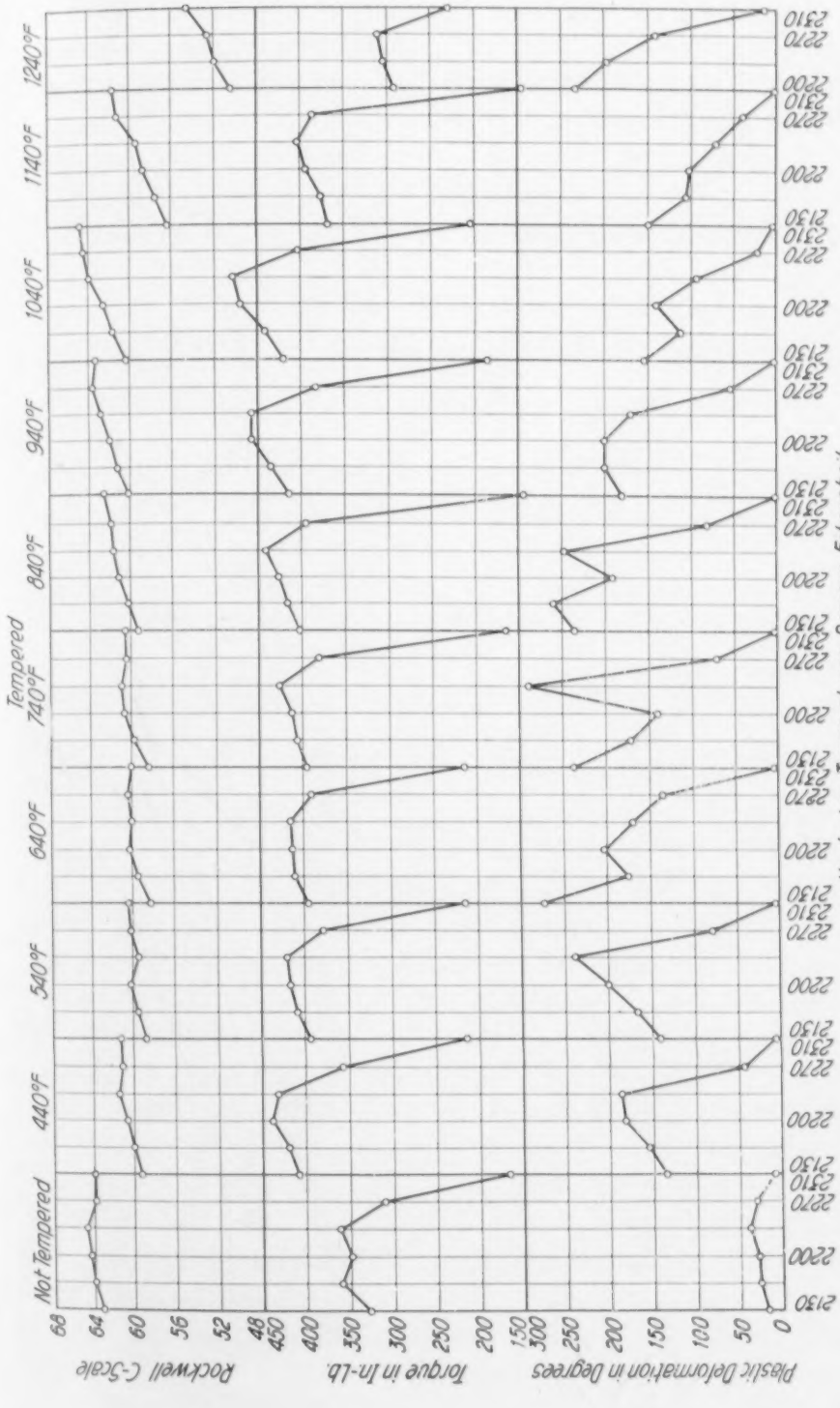


Fig. 13—Steel XII, (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

Fig. 14—Steel XII, (Upper Set of Curves) Rockwell Hardness versus Hardening Temperatures; (Middle Set of Curves) Ultimate Torque versus Hardening Temperatures; (Lower Set of Curves) Plastic Deformation versus Hardening Temperatures.

tions between the maxima and the minima which characterize the corresponding curves of Steel IV. They more nearly resemble the corresponding curves of Steel XXII (18-4-1) but have a lower plasticity at the peak of strength.

Full details of the response to heat treatment of the remainder of the steels in Table II will not be given. Some of their most noteworthy characteristics are summarized in Table V and commented on as follows:

Steel X having the lowest alloy content, also has the lowest strength, hardness and plasticity of any of the steels of this type.

Table II

Molybdenum High Speed Steel, Tungsten Bearing, with from 15 Per Cent to 30 Per Cent as Much Tungsten as Molybdenum

Steels	Carbon	Chromium	Tungsten	Vanadium	Molybdenum	Ratio(a)	Ratio W — Mo. (b)	Tungsten Equivalent(c)
X	0.61	3.65	1.69	1.00	6.67	2.4	25.3	15.03
XI	0.68	3.96	2.01	1.04	7.10	2.3	28.3	16.22
XII	0.66	3.53	1.99	1.00	8.20	2.0	24.2	18.39
XIII	0.78	5.25	2.06	1.01	8.18	1.9	25.2	18.42
XIV	0.90	3.33	1.59	1.66	9.65	1.7	16.5	20.89
XV	0.76	3.82	1.67	1.01	11.05	1.5	15.2	23.77

(a) The product of this ratio and the molybdenum content is equivalent to approximately 18 per cent tungsten.

(b) This is the per cent of tungsten with reference to the molybdenum content.

(c) This tungsten equivalent is based upon the common assumption that one per cent of molybdenum is equivalent to two per cent of tungsten.

Its properties correspond more nearly to those of Steel XXI (15-4-1), a tungsten high speed steel also of low alloy content. It is observed that it has a higher strength, a similar hardness and a lower plasticity than Steel XXI.

Steel XI having a higher chromium and a lower molybdenum than Steel XII, has properties quite similar to it except that it shows a high plasticity. It is noted that the maxima of the mechanical properties as noted in Table V, are on a par with those of Steel XXII, as shown in Table VI.

Steel XIII having a higher carbon and chromium content, has similar properties to those of Steel XII, with somewhat lower strength and higher hardness. Its maximum secondary hardness is definitely above that of Steel XXII.

Steel XIV has higher carbon and molybdenum with lower tungsten. Its strength is on a par with that of Steel XXII. Its maximum

Table III

Miscellaneous Compositions of Molybdenum and Tungsten High Speed Steels

Steels	Carbon	Chromium	Tungsten	Vanadium	Molybdenum	Cobalt	Nickel	Ratio(a)	Tungsten Equiv. (b)	Ratio W/Mo. (c)
XVI	0.75	3.91	4.01	1.12	8.17	None	None	1.7	20.35	49.1
XVII	0.66	4.32	0.04	1.18	10.29	9.11	None	1.8	20.62	0.4
XVIII	0.69	3.51	None	1.01	6.46	3.88	None	2.9	12.92	..
XIX	0.71	4.18	None	1.01	5.94	None	2.04	3.0	11.88	..
XX	0.77	4.09	12.47	0.77	2.14	None	None	2.6	16.75	582%
XXI	0.67	3.80	14.45	0.63	None	None	None	..	14.45	..
(d) XXII	0.69	3.72	18.17	1.00	None	None	None	..	18.17	..

(a) The product of this ratio and the molybdenum content is equivalent to approximately 18 per cent tungsten.

(b) This tungsten equivalent is based upon the common assumption that one per cent of molybdenum is equivalent to two per cent of tungsten.

(c) This is the per cent of tungsten with reference to the molybdenum content.

(d) This is an 18-4-1 type studied previously (4).

secondary hardness is the highest observed in any of the experiments here recorded. Its plasticity is low.

Steel XV having higher carbon and very high molybdenum has a lower maximum strength, similar hardness and higher plasticity than Steel XII.

Photomicrographs illustrating the structures of some steels of this type at their maxima of strength are as follows:

Fig. 15, shows Steel XII. This structure is typical of a hardened and tempered high speed steel. (Note the similarity to Fig. 11).

Fig. 16, shows Steel XIV. It is also a typical high speed steel structure but shows finer austenitic grains and finer martensitic markings, with less of the dark troostite outlining the martensitic "worms," than is usually observed. The carbides are small and well distributed. This structure has a remarkable combination of high hardness, and great strength, as shown in Table V.

Fig. 17, shows Steel XV. The austenitic grain size is normal. The martensitic structure is fine and vermiform. The carbides are present in considerable quantities, gathered for the most part in large masses. There is some evidence of unusual troostitic development in spots which may be the beginning of a scarcity of carbon. This would be caused by the high molybdenum content withdrawing carbon from solution to form carbide.

The data obtained on the performance of the steels of Table II, are shown in the last column of Table V. Again it is observed, that the performance ratings of the various steels do not bear a direct relation to any of the mechanical properties recorded. It is also ob-

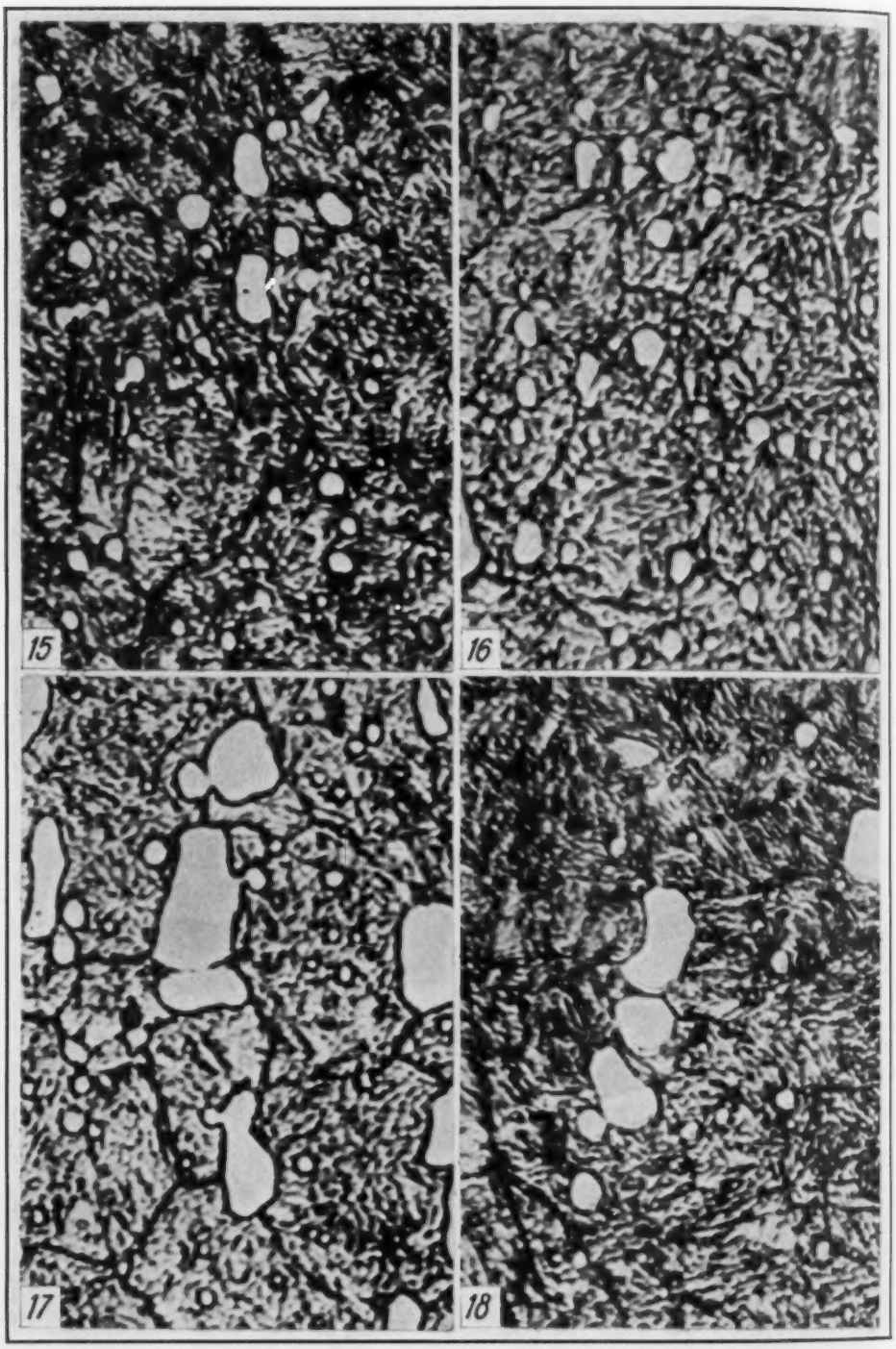


Fig. 15—Steel XII, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 2000.

Fig. 16—Steel XIV, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 2000.

Fig. 17—Steel XV, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 940 Degrees Fahr. × 2000.

Fig. 18—Steel XVI, Structure at the Maximum Strength, Hardened at 2235 Degrees Fahr. (1225 Degrees Cent.), Tempered at 1040 Degrees Fahr. × 2000.

Table IV
Summary of the Mechanical Properties and the Performance of the Molybdenum High Speed Steels, Tungsten-Free

Steels	Maximum Secondary (a) Strength	Maximum Secondary (b) Hardness	Plasticity at Maximum (c) Strength	(d) Fracture Coarsens °F	°C	Performance Rating (e)
I	429	64.6	95	2270	1240	64
II	429	63.3	147	2270	1240	76
III	429	65.7	111	2270	1240	33
IV	443	65.8	108	2270	1240	43
V	f	...	...	2290	1250	66
VI	f	...	...	2290	1250	62
VII	411	65.9	41	2310	1265	60
VIII	467	65.5	51	2290	1250	91
IX	268	54.8	75	2325	1275	g

The average performance rating, of the eight steels of this type tested, is 62 per cent.
(a) In pounds torque at one inch radius.
(b) Rockwell C scale.
(c) Plastic deformation in degrees of twist.
(d) Approximate hardening temperature at which the fracture becomes coarse with a soaking time of thirty seconds.
(e) In percentage of the drilling performance of the 18-4-1 type of steel.
(f) The material available was not sufficient for an examination of the mechanical properties on these steels.
(g) No drilling tests were made upon this steel. It is believed from the mechanical properties observed that if tried, the performance rating would approach zero.

served that the performance is not directly in proportion to variations in the "tungsten equivalent," as calculated by the most commonly known ratio of one molybdenum to two tungsten, and shown in the last column of Table II. Brief comments upon the performance of the individual steels are as follows:

Steel X, has a low alloy content. Its physical properties resemble those of Steel XXI (15-4-1) so that it is comparable with this low tungsten type of high speed steel. The performance rating of Steel X is 83 per cent, as against 55 per cent for Steel XXI. This indicates a surprising amount of cutting quality for such a low alloy steel.

Steel XI, has a somewhat higher molybdenum content and physical properties which make it comparable to the 18-4-1 type. Its performance rating of 94 per cent indicates that it is indeed in that class.

Steel XII with considerably higher molybdenum, and the highest strength recorded in these experiments, has a performance rating of 88 per cent. This drop in performance indicates that the strength is not the only factor controlling cutting quality.

Steel XIII, has a high carbon and a high chromium content. Its strength is fair and its hardness is high. The performance rating is 113 per cent. There is not yet sufficient data at hand to say definitely to what extent this increase in performance was due to the variation of the carbon and the chromium contents.

Steel XIV is characterized by higher molybdenum and much higher carbon. Its strength is good, its hardness very high and its plasticity low. Its performance rating is 104 per cent.

Steel XV, has very high molybdenum with moderately high carbon. Its strength is only fair, its hardness good, and its plasticity moderately high. Its performance rating is also 104 per cent.

Looking at the preceding six steels as a type, it is apparent that they are entitled by their performance to consideration in the same class as the familiar types of tungsten high speed steels.

Limits of Analyses Range

It has not as yet been possible to determine definitely the exact range of analyses which limit this type. A general idea as to the low limit for tungsten is obtained by the results upon the steels in Table I. In order to investigate the high limit for tungsten, experiments were conducted upon Steel XVI shown in Table III. This steel contains about 4 per cent tungsten or about 49 per cent as much tungsten as molybdenum. As the mechanical properties of this steel have shown distinct departures from the conventional data, it is desirable to show them in detail. The schedule of heat treatments is as follows, each "X" representing a heat treatment given to duplicate specimens. The hardening temperatures were planned to cover a higher range than used for the steels in Table II, because it was thought probable that the high tungsten content would raise the permissible hardening temperatures.

	Tempering Temperatures									
Hardening Temperatures	Not Tempered	440° F (225° C)	540° F (280° C)	640° F (340° C)	740° F (395° C)	840° F (450° C)	940° F (505° C)	1040° F (560° C)	1140° F (615° C)	1240° F (670° C)
2200° F (1205° C)	X	X		X	X	X	X	X	X	X
2235° F (1225° C)	X	X		X	X	X	X	X	X	X
2270° F (1240° C)	X	X		X	X	X	X	X	X	X
2310° F (1265° C)	X	X		X	X	X	X	X	X	X
2345° F (1285° C)	X	X		X	X	X	X	X	X	X

The data from the observations upon the mechanical properties are found in the curves shown in Figs. 19 and 20. The duplicate speci-

Table V

Summary of the Mechanical Properties and the Performance of the Molybdenum High Speed Steels, Tungsten-Bearing, with from 15 Per Cent to 30 Per Cent as Much Tungsten as Molybdenum

Steels	Maximum Secondary (a) Strength	Maximum Secondary (b) Hardness	Plasticity at Maximum (c) Strength	(d) Fracture Coarsens °F	°C	Performance Rating (e)
X	439	64.6	76	2290	1250	83
XI	476	65.3	216	2290	1250	94
XII	478	64.8	94	2290	1250	88
XIII	462	66.3	85	2290	1250	113
XIV	470	67.6	78	2310	1265	104
XV	449	65.1	147	2325	1275	104

The average performance rating, of the six steels of this type tested, is 98 per cent.

(a) In pounds torque at one inch radius.

(b) Rockwell C scale.

(c) Plastic deformation in degrees of twist.

(d) Approximate hardening temperature at which the fracture becomes coarse with a soaking time of thirty seconds.

(e) In percentage of the drilling performance of the 18-4-1 type of steel.

Table VI

Summary of the Mechanical Properties and the Performance of the Miscellaneous Molybdenum and Tungsten High Speed Steels in Table III

Steels	Maximum Secondary (a) Strength	Maximum Secondary (b) Hardness	Plasticity at Maximum (c) Strength	(d) Fracture Coarsens °F	°C	Performance Rating (e)
XVI	443	67.2	38	2290	1250	64
XVII	471	66.7	54	2310	1265	68
XVIII	435	66.0	73	2270	1240	39
XIX	410	65.3	89	2270	1240	33
XX	429	64.4	67	2290	1255	63
XXI	425	64.7	144	2360	1290	55
XXII	469	65.4	145	2415	1325	100

(a) In pounds torque at one inch radius.

(b) Rockwell C scale.

(c) Plastic deformation in degrees of twist.

(d) Approximate hardening temperature at which the fracture becomes coarse with a soaking time of thirty seconds.

(e) In percentage of the drilling performance of the 18-4-1 type of steel.

mens have been averaged to obtain the value plotted. These curves are to be compared particularly with those for Steel XII in Figs. 13 and 14.

The hardness curves are similar in shape to those of Steel XII, but show considerably higher hardness, both before tempering and at the maxima of secondary hardness.

The strength curves are also similar in shape to those of Steel XII but uniformly show much lower strength.

The plasticity curves also show some similarity of shape but

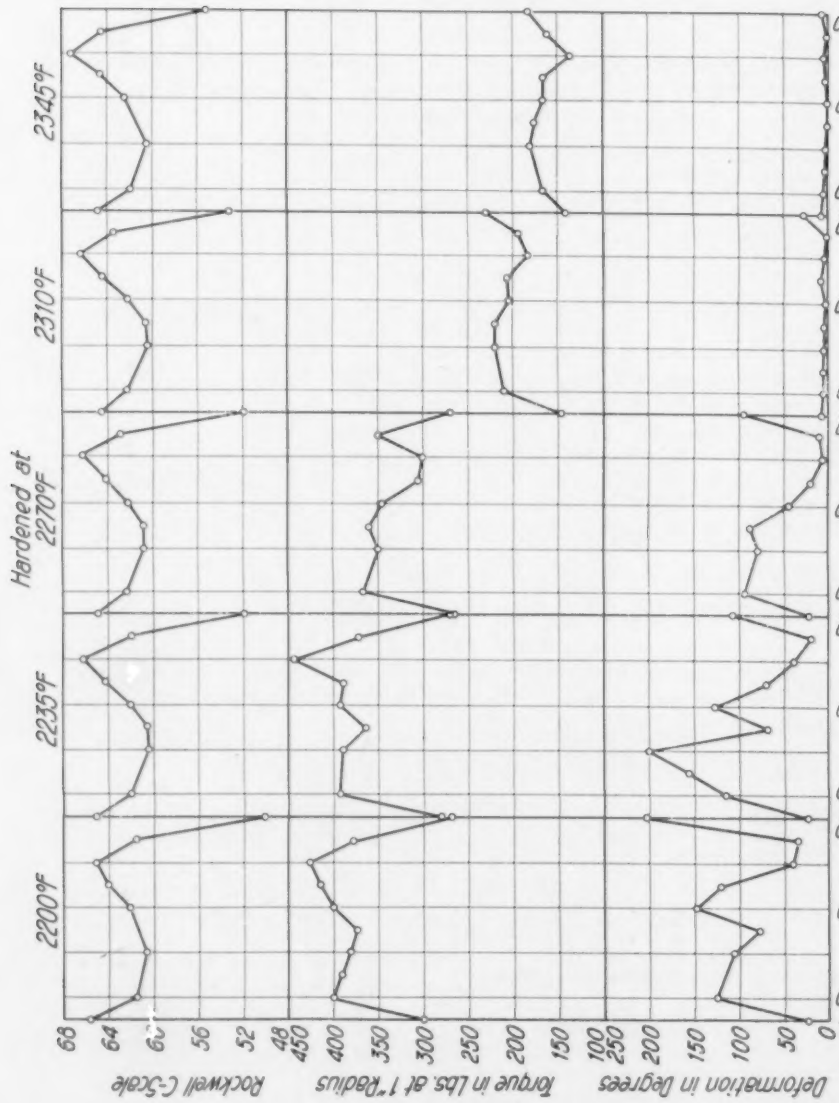


Fig. 19.—Steel XVI. (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

the curves for Steel XVI are the more erratic while the general plasticity has been lowered to such an extent that the steel must be characterized as brittle.

A photomicrograph illustrating the structure of Steel XVI at the maximum of strength is shown in Fig. 18. The austenitic grains are large but indistinct. The martensitic structure is partly vermiform but has a strong tendency toward the development of straight needles which are coarser than those in Figs. 11, 15, 16 and 17. The carbides are in large rounded masses. The coarse structure of the martensite probably contributed to the brittleness of this type of steel. The

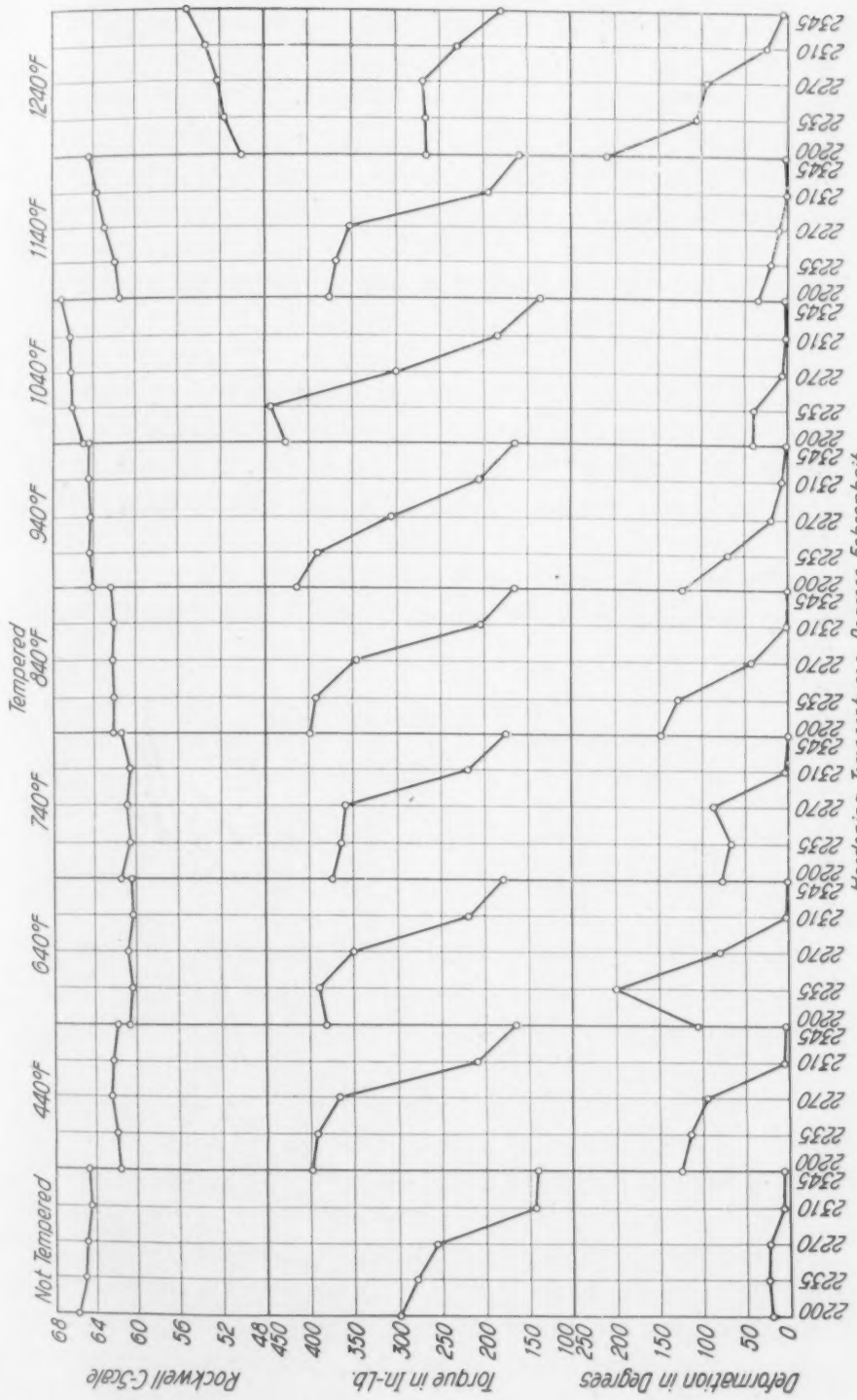


Fig. 20—Steel XVI, (Upper Set of Curves) Rockwell Hardness versus Hardening Temperatures: (Middle Set of Curves) Ultimate Torque versus Hardening Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

Fig. 19—Steel XVI, (Upper Set of Curves) Rockwell Hardness versus Tempering Temperatures; (Middle Set of Curves) Ultimate Torque versus Tempering Temperatures; (Lower Set of Curves) Plastic Deformation versus Tempering Temperatures.

expectation that the range of permissible hardening temperatures would be raised, was only slightly realized.

The performance of this steel as shown in the last column of Table VI is 64 per cent. This low rank appeared to be largely due to the chipping and crumbling of the cutting edges caused by the excessive brittleness.

Effect of Small Molybdenum Additions to Tungsten High Speed Steels

In Steel XX the relative amounts of tungsten and molybdenum are about reversed from the proportions used in the steels of Table II. It was desired to determine if the beneficial effects so outstanding in the high molybdenum steels of Table II would also be found if the proportions were reversed. Full details as to the mechanical properties will not be given but from the data in Table VI it is observed that while the hardness is normal, the strength, plasticity and cutting quality are low.

Summary

Tungsten-Free Molybdenum Steels

In a study of the observations upon the straight molybdenum high speed steels listed in Table I, the following remarks seem pertinent.

The most favorable range of hardening temperatures is from 100 to 150 degrees Fahr (55 to 85 degrees Cent.) lower for molybdenum than for tungsten high speed steels.

The melting point of the carbides in the molybdenum steels as evidenced by the formation of eutectic skeletons, is also about 150 degrees Fahr. (85 degrees Cent.) lower than for the tungsten steels.

The molybdenum steels develop their secondary hardness and strength at about the same tempering temperatures as the tungsten steels. There is some evidence that the range of both hardening and tempering temperatures in which the best properties are developed, is slightly narrower for the molybdenum than for the tungsten steels.

The molybdenum steels are in general equal in hardness to the tungsten steels but lower in strength and plasticity. The martensitic structure of the molybdenum steels is frequently coarser than in the tungsten steels. For similar carbon contents the molybdenum steels

show fewer carbides in the structure than the tungsten steels. If the carbon content of the molybdenum steels is increased to the point where a normal amount of carbides appear in the structure, the strength and the cutting quality both seem to be improved.

Additions of cobalt and nickel did not appear to improve either the mechanical properties or the cutting quality.

In cutting quality the molybdenum steels are definitely below the tungsten steels. The average performance rating of the steels in the Group No. I to VIII being only 62 per cent of that of the 18-4-1 type.

It would appear that sufficient reasons are here found to account for the well known lack of commercial popularity encountered by this type of steel in the past.

Tungsten Bearing Molybdenum Steels

The type of molybdenum high speed steel with an auxiliary tungsten content of about 25 per cent of the total amount of molybdenum present, may be commented on as follows:

The tungsten addition has had a slight effect toward raising the hardening temperatures at which the most desirable properties are developed. It has also slightly raised the hardening temperature at which a coarse fracture appears.

It has had a pronounced effect in reducing the size of the martensitic needles and in converting them from the straight needle to the distorted or vermiform type. It has not affected the hardness materially. It has definitely increased the strength. It has smoothed out some of the wide fluctuations in plasticity which have been characteristic of the tungsten-free steels. It has effected a pronounced improvement in the cutting quality, the average performance rating of Steels X to XV inclusive being 98 per cent.

There appears to be a limit to the amount of tungsten which can be advantageously employed in a molybdenum steel of this type. In Steel XVI, while a high degree of hardness was produced by a tungsten addition to the amount of about 50 per cent of the molybdenum present, it was accompanied by great brittleness and poor performance.

Investigation of combinations of tungsten and molybdenum in other proportions such as tried in Steels XVI and XX have as yet failed to produce favorable results.

It is believed that in this type of steel some of the most important limitations which have prevented the commercial development of molybdenum high speed steels in the past have been either greatly reduced or entirely eliminated.

Conclusions

A general conclusion is that the property of a high speed steel known as "cutting quality" is complex and that it cannot be defined in terms of any single mechanical property here investigated.

With reference to the tungsten-free molybdenum steels, it is concluded as a result of these experiments that they have a cutting quality definitely below that of the standard 18-4-1 type of steel. Their performance seems to be more nearly on a par with the 15-4-1 type of tungsten high speed steels.

A new type of high speed steel has been developed in which molybdenum is the principal alloying element and to which has been added about one-fourth as much tungsten as molybdenum. The other alloying elements are those commonly found in high speed steels and in the usual proportions. The addition of such an auxiliary amount of tungsten has been found to improve the microstructure and the strength, to make the plasticity more uniform and particularly to greatly increase the cutting quality. The cutting quality of this type as measured by drilling tests greatly exceeds that of any other molybdenum steels previously examined, and at least approaches that of the 18-4-1 type of tungsten steels. The beneficial effects of the addition of this small amount of tungsten is materially greater than can be explained upon any basis of the equivalency of the two elements.

It is further concluded that the statement so common in the literature that "molybdenum will replace tungsten in high speed steel in the proportion of one to two," is much too broad and also that it leaves much unsaid. The behavior of the two elements is here shown to be different in a number of important particulars. Their behavior is particularly different when both are present in the same steel. There appears to be no simple ratio in which they may be substituted for each other, either as a whole or in part, to produce a uniform cutting quality. The original belief which led to this investigation has now been confirmed, that is—*molybdenum high speed steels have an individuality of their own.*

From a study of these results, it seems reasonable to predict that molybdenum high speed steels will find a field of usefulness in industry on their own merits.

It is realized that the results above reported are incomplete and that there are many gaps to be filled. It is presented only as a single stone in the foundation of our knowledge of high speed steels.

Acknowledgment is made of the assistance of the Sanderson Works of the Crucible Steel Company of America, who have executed the specifications of the author on many of the compositions of steel used in the experiments here reported.

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4. J. V. Emmons, "Some Physical Properties of Hardened Tool Steel," *Proceedings,* American Society for Testing Materials, Vol. 31, Part II, 1931, p. 47.
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DISCUSSION

Written Discussion: By Frank Garratt, Universal Steel Co., Bridgeville, Pennsylvania.

The society is again to be congratulated on hearing from Mr. Emmons a paper of his usual quality. The subject which he discusses should be of great interest to all users of cutting steels, and is of particular interest to the speaker, since it confirms in many respects conclusions we have made regarding molybdenum cutting steels.

We were impressed some time ago with the vulnerable position tungsten occupies in the high speed steel industry, and in view of the generally admitted fact that molybdenum was of considerable value in certain cutting steels, it seemed somewhat surprising that the element had not come into wider use in steels of the high speed type. Realizing that it had great possibilities as a strategic metal, and that its use should eliminate wide price fluctuations in tungsten steels in times of national stress, it was determined to learn why molybdenum steels had had so little permanency in the various commercial efforts that had been made to exploit them.

Our early work emphasized that steels in which molybdenum entirely replaced tungsten were distinctly unreliable, a fact which seems to be well known to those who have worked with molybdenum high speed steels. It

was only natural to investigate added elements that would give the steels the stability they required, and after some experimentation it was decided that tungsten showed more promise than any of the elements that were investigated. It was found that when tungsten was added in certain limited proportions a reliable steel of considerable merit could be produced. There was, therefore, finally produced a "base" composition that was found to be fully the equal of the 18-4-1 type of tungsten steel that is today considered the "base" composition of the tungsten steels. The molybdenum-tungsten cutting steel so developed is now being marketed in substantial quantities, and a chemical analysis of an average sample will show the following typical composition:

	Per Cent
Carbon	0.77
Tungsten	1.75
Molybdenum	7.75
Chromium	4.10
Vanadium	1.05

It will be observed that this composition is quite similar to those which Mr. Emmons has independently found to give best results in his drilling tests, and it is particularly gratifying to be able to confirm his results. The fact that independent workers on this problem have arrived at substantially the same result would indicate that steels of the above composition have considerable merit.

Since our work has indicated that only the molybdenum-tungsten types of steels can be seriously considered as rivals of the 18-4-1 type of tungsten steels, we are confining our discussion of Mr. Emmons' results to his steels X to XVI. Mr. Emmons has selected XII as being representative of the molybdenum-tungsten type. While this particular composition has given fairly good results, in comparison with 18-4-1 tungsten steels, our work has led us to believe that it would have shown better cutting results had the carbon been somewhat higher. It has been our experience that the effectiveness of cutting tools made from these steels falls off rapidly as the carbon drops below 0.70 per cent, and it is of interest to note that Steels X, XI, and XII, containing 0.68 per cent carbon, or less, do not give as good cutting results as Steels XIII, XIV, and XV containing 0.76 per cent carbon, or over. It is questioned whether the variations in the percentages of the other elements shown have had as profound an influence on the cutting properties as the varying percentages of carbon. Mr. Emmons' average results with this group of steels show about the same performance as the standard 18-4-1 tungsten steel. It is of interest in this connection to know that over the past several years we have made several hundred tests on steels conforming rather closely to the typical composition to which I have previously referred. Comparisons have been made in all cases with various brands of standard 18-4-1 tungsten steels, and the average performance of all the molybdenum-tungsten steels thus far tested is definitely better than the best 18-4-1 type of tungsten steel which we have tested. Service tests are confirming the results which have been obtained in a laboratory way.

It might be considered unusual that Steel XVI, containing 4 per cent tungsten should fall off so rapidly in cutting performance, but here again Mr. Emmons' results have confirmed our conclusions that tungsten additions substantially in excess of 2 per cent are detrimental rather than helpful. Torsion tests show the decided lack of toughness of Steel XVI in the hardened condition, and this fact quite likely accounts for its poor cutting performance. It is also believed that the microstructure of the 4 per cent tungsten steel, as well as those steels of high molybdenum content, is quite significant. It will be observed that the carbides tend to be quite massive, and it is difficult to see how such steel can be as satisfactory as Steels XII or XV, where the carbide distribution is so uniform.

It has been our experience that the molybdenum-tungsten steels which are now being marketed are hardened most satisfactorily at temperatures of around 2175 to 2200 degrees Fahr. These temperatures are somewhat lower than those given in Mr. Emmons' paper, but it is appreciated that the desirable hardening temperatures will vary with the preheating temperatures employed, the holding time at hardening temperature, the type of hardening equipment used, and other conditions attending the hardening practice. It is believed, however, that hardening temperatures much in excess of 2200 degrees Fahr. will be found somewhat risky for most hardening practices, owing to the ready tendency for the carbide eutectic to form. This is referred to by Mr. Emmons on page 218 of his paper in which he calls attention to the lower melting points of the carbides occurring in molybdenum steels.

The usual types of hardening equipment are quite suitable for handling molybdenum-tungsten steels, and the fact that comparatively low hardening temperatures are used is a distinct advantage. It is also worthy of mention that annealing temperatures need not be as high as commonly employed for tungsten high speed steels, and annealed material can be more readily machined than the tungsten steels.

Those who have worked with molybdenum-tungsten steels of the type discussed are impressed with the possibilities of these materials, and it is believed that metallurgists will find them a fruitful field for research. The speaker believes that progress with such steels has been retarded because they have been viewed too much in the light of tungsten high speed steels. Mr. Emmons has well expressed this when he states that "molybdenum high speed steels have an individuality of their own". It should be kept in mind that the steels contain considerably less alloying content than tungsten high speed steels, and heat reactions are therefore free from the sluggishness of the latter steels.

It should be obvious that steels of such promise will find wide application in industry. They are of, at least, equal quality when compared with tungsten steels, and are more economical to produce because of their lower alloy content; they have an inherent price advantage over tungsten steels because of their lighter weight, and it is believed that they offer new possibilities in untried compositions yet to be developed.

Written Discussion: By John A. Mathews, vice-president, Crucible Steel Company of America, New York City.

This paper constitutes a very important supplement to Mr. Emmons' papers of last year referred to at the end of the paper. It gives evidence of the same

careful methods of investigation that were used in his earlier published papers.

The steels are not so familiar to the general public as the 18-4-1 steel dealt with so extensively last year. Mr. Emmons, however, calls attention to the fact that molybdenum high speed steels have been known almost as long as those made with tungsten. I am not sure but that in this country they have been known fully as long as the tungsten products. The Crucible Steel Company of America manufactured a molybdenum air hardening tool steel beginning about 1896. This type of steel had a considerable sale up until the introduction of high speed steel early in this century following upon the classic investigation of Taylor and White.

When molybdenum was almost a chemical curiosity to the general public we were using about 50 tons per year some 30 years ago. In a paper on molybdenum steels presented before the American Institute of Mining Engineers in 1921 I outlined somewhat the history of the use of molybdenum in this country, referring particularly to the early attempts at making high speed steel with molybdenum instead of tungsten.

Our first steel containing both molybdenum and tungsten was made in 1902. We investigated molybdenum thoroughly as a substitute for tungsten in permanent magnet steel at about the same time. The difficulties with molybdenum high speed steel as made in the early part of the century are pretty well known, particularly those arising from the decarburization and demolybdenization of the surface when the material is subjected to elevated temperatures. In the old days when passing through the hammer shops we could tell what hammers were working on molybdenum steel by reason of the yellow fumes arising from it,—the fumes presumably consisting of volatile trioxide.

A distinguished foreign metallurgist stated that molybdenum steels containing about 6 per cent molybdenum could not be rolled. At the very time this statement was made we were rolling large quantities of material containing 9 per cent of molybdenum and later on successfully rolled steel containing up to 15 per cent of molybdenum.

Mr. Emmons has referred to the important investigation at Watertown Arsenal under the direction of Captain S. B. Ritchie, and his most important contribution was in working out a method for heating and hardening the steel without producing a surface softness. From a military point of view, molybdenum is looked upon as a strategic element of which we possess an ample supply in our own country. The same cannot be said for tungsten.

From time to time since 1902 we have manufactured various modifications of molybdenum high speed steel, including tungsten, cobalt and vanadium as additional elements. This work was done on the general assumption that the art of manufacture was progressing all the time and that some day our national supply of molybdenum might be called upon for the manufacture of high speed steel. I was in touch with the work done at Watertown Arsenal during its progress and before the publication of the results.

In the case of one steel only tested by Mr. Emmons is there a substantial improvement over the standard 18-4-1, and in this steel XIII I note the chromium content is about 1.5 per cent higher than in the general run of the steels. It might be inquired to what extent this increase in chromium accounted

for the results rather than the tungsten addition or supplementing the tungsten addition.

Captain Ritchie in his paper I believe specifically states that his attempts at making high speed steel drills from his molybdenum product were not successful, and certain other tool manufacturers have attempted it from time to time, even including a type of steel containing about one-fourth as much tungsten as molybdenum, but without obtaining results at all approaching those of the 18-4-1. And the same might be said for its use in other directions and for other types of tools.

We have been particularly interested in Mr. Emmons' work because we supplied a large part of the steels discussed in this paper and because of our general interest in the subject of molybdenum for so many years. The 18-4-1 used as a standard for comparison with the experimental steels was in fact the result of the determination of this company to abandon molybdenum steels in behalf of tungsten steels about 1903 or 1904. Our general experience with molybdenum steel and its various modifications is that it is not as fool-proof as 18-4-1. On occasions it gives very satisfactory results, but with more tendency to brittleness,—particularly in lathe tools, and it also seems to require greater skill in its heat treatment.

The method of Captain Ritchie for preventing decarburization while effective, is not a process we would care to use if it were not absolutely necessary. It is what one might call a bit messy, and the free use of borax in heating furnaces will not help to keep them clean when other products are to be handled, while the molten borax under the hammer is apt to spatter to the discomfort of the hammer crew.

Mr. Emmons' work is so thorough and inclusive that it will save future workers a great deal of time and trouble, and we are glad to have been able to participate in this valuable contribution to tool steel metallurgy.

Written Discussion: By Alan Kissock, Climax Molybdenum Co., New York City.

I have read this paper with much interest, and am of the opinion that Mr. Emmons has presented the facts about as we know them today. Aside from the early work that was done along these lines it is only recently that any attempts have been made to utilize molybdenum in this class of steel. The actual success which has been met in service from these rather limited researches would appear to warrant a careful study in the strong belief that from such an investigation an improved and worthwhile product might result.

Written Discussion: By Dr. Michael G. Yatsevitch, Watertown Arsenal, Watertown, Mass.

Mr. Garratt, in his discussion of Mr. Emmons' paper, mentions that their "early work emphasized, that steels in which molybdenum entirely replaced tungsten were distinctly unreliable, a fact, which seems to be well known to those who have worked with molybdenum high speed steels". It seems to me important to note, that such a strong and indefinite expression as "distinctly unreliable", gives very little idea about the actual properties involved, and at the same time may unnecessarily frighten away possible users of molybdenum steels. Only the actual facts, stated as exactly as possible, can be of real help

in the proper solution of every engineering problem, without involving superfluous and expensive speculations.

The experiments at the Watertown Arsenal and the work of Arnold and Polzguter, carried out in 1922 and 1923 respectively, proved that the outstanding difference of molybdenum high speed steels as compared with tungsten steels lies in a somewhat greater susceptibility to oxidation at higher temperatures, greater difficulty in forging, and also in greater sensitivity in heat treatment. However, the rapid progress made in recent years in heating furnaces, technique of heat treatment and the mechanical working of steel, made the elimination of the difficulties, caused by the above properties, surprisingly easy, thus facilitating for molybdenum tool steels the road to the everyday market.

Since the World War the Ordnance Department of the U. S. Army has been actively interested in the substitution of molybdenum for tungsten in high speed steels, in whole or in part, because tungsten belongs to the group of so-called "strategic materials." The Department's investigations were carried out at the Watertown Arsenal and were published in part in the "Army Ordnance Magazine" in January, 1930. The investigations proved, that tools completely satisfactory for present day practical purposes in high speed work could be made by the substitution of molybdenum for tungsten. The investigations in general were somewhat more comprehensive than those of Mr. Emmons, since they involved the development of the technological side of making the metal, the stock and the tools, including forging, rolling and heat treatment practice.

More than a year ago, after proving by extensive laboratory and shop investigations at the Arsenal, the complete suitability of molybdenum as a substitute for tungsten in tool steels, the Ordnance Department placed with one of the manufacturers of high speed steels an order for 14,000 pounds of molybdenum tool steel of specified composition:

C	Mn	Si	S	P	Mo	Cr	V
0.65-0.75	0.15-0.25	0.15-0.25	each below	0.025	9.25-9.75	3.25-3.75	1.15-1.35

made into various shapes, of sizes ranging from $\frac{3}{8}''$ to $6''$ in diameter, or other corresponding dimensions. The whole lot was distributed among various arsenals of the U. S. Army Ordnance Department to be made into various tools for use in production work under the condition of strict following and registration of the performance obtained. The data accumulated from that experiment on a production scale wholly confirmed the expectations and hopes built on the experimental work. It appeared that the manufacture (particularly the rolling) of the steel and shapes did not present any difficulties: on the contrary, the manufacturers were very pleasantly surprised at the ease with which all the difficulties, anticipated and feared at the time of taking the contract, were eliminated, the Arsenal naturally cooperating with the manufacturer in all respects, passing on all information obtained from the previous investigation.

In general the Watertown Arsenal tools gave service performances much more favorable to molybdenum tools than might have been expected from the results of Mr. Emmons for similar compositions. It was realized that the drilling tests alone do not represent a true test for tools, so the actual shop tests on heavy and light lathe and planer tools, milling cutters and reamers

were selected and preferred. Similar parallel tests were made with tungsten tools (of 18-4-1 type) and performances were compared. It appeared that light and particularly heavy planer and lathe tools stood up on an average as well or better than the tungsten or tungsten-cobalt tools.

Steels VI and VII in Mr. Emmons' series are the nearest to the Watertown Arsenal steels in composition. It is a pity that Steel VI was not tested for mechanical properties, and that no curves are given for Steel VII. This makes a close comparison of the Arsenal steel with Mr. Emmons' steels impossible.

The Arsenal heat treatment differs somewhat from that of Mr. Emmons, and perhaps it may throw some light on differences in properties and structure. The heat treatment and photomicrographs and other more detailed information are given in the written discussion by Colonel Jenks.

I personally wish to join in commending Mr. Emmons for the elegant piece of engineering research described in his paper. It seems to represent a part of one of the very few and rare investigations tending to establish quantitatively the difference in the effect of molybdenum and tungsten on the high speed cutting properties of tool steel. Since 1913 this subject has appeared to me to be of particular value and interest in view of the general chemical and physical properties of both elements, and seem to promise some tempting generalizations, which could be of great practical value generally in perfecting and designing of "inventing" new high speed steels. The appearance of investigations of the character like the one presented by Mr. Emmons ought to be much welcomed and encouraged, because they always precede an important, definite and general advance in some line of engineering.

Written Discussion: By G. F. Jenks, Lt. Col., Ord. Dept., Watertown Arsenal, Watertown, Mass.

The Ordnance Department of the U. S. Army has been interested in the substitution of molybdenum for tungsten in whole or in part because tungsten is a strategic metal.

Mr. Emmons' work confirms the Department's experience that, through partial or complete substitution of molybdenum for tungsten in usual tool steel compositions, we need no longer face the danger of a shortage of tool steels even if we were cut off entirely from foreign sources of tungsten. The Department's investigations were carried out at Watertown Arsenal and were published in part in a paper published in *Army Ordnance* in 1930.[1]

There was not much attention given to combinations of molybdenum and tungsten. Most of the results obtained regarded complete substitution. The study was carried to a point which indicated that satisfactory tools could be made from molybdenum steels. This investigation was somewhat more comprehensive than that of Mr. Emmons since it involved development of foundry, forging, and rolling practice as well as heat treatment. Since Mr. Emmons has emphasized combinations of molybdenum and tungsten, some review of this work may be of interest.

The Watertown Arsenal tools gave service performances more favorable

[1]S. B. Ritchie, "Molybdenum in High Speed Steel," *Army Ordnance*, Vol. XI, No. 61, p. 12, 1930.

to the molybdenum tools than might be expected from the results of Mr. Emmons for similar compositions. This more optimistic picture may have been due to the fact that, while Mr. Emmons' results are based on drilling tests alone, the Watertown tools were given actual shop tests as lathe and planer tools, milling cutters and reamers. The tools were in service in a number of government shops in competition with best obtainable commercial tools and were tested by various commercial companies. One series of drilling tests was carried out by the Cleveland Twist Drill Company. These drilling tests were unfavorable, and were the only very unfavorable reports of performance received. This unfavorable report in the light of the present paper may be due to inherent lack of quality in molybdenum tool steels. However, the steel furnished by the Arsenal for the drilling tests was not of quite the composition found to give best results in other tool forms; this fact may have contributed to the poor performance. Heavy planer and lathe tools stood up on the average as well as or better than tungsten or tungsten-cobalt tools with which they were compared.

Similar tests were made for small lathe tools, milling cutters, reamers, etc. In all cases the molybdenum tools compared very favorably with the similar tungsten tools employed on the same work.

In Mr. Emmons' series, Steels VI and VII most closely approximate the Watertown composition that was found to perform best in service. Due to lack of material, Steel VI was not tested for mechanical properties. The composition of VII together with that of the Watertown steel is given below:

	C	Mn	Si	Cr	Mo	V	W
Watertown	0.68	0.25	0.25	3.50	9.50	1.25	none
Emmons VII	0.66	not reported	not reported	4.26	10.19	1.14	0.10

Curves for Steel VII are not given, but it is remarked that they were surprisingly similar to those of Steel IV which are given.

The Watertown steel was found to give better performances when quenched from a little below the hardening range Emmons regards as most favorable. That is, he finds for these steels maximum secondary strength when hardening at around 1235 degrees Cent. (2255 degrees Fahr.) and tempering at around 560 degrees Cent. (1040 degrees Fahr.). The Watertown steels were quenched from 1175 to 1200 degrees Cent. (2150-2190 degrees Fahr.) and tempered at from 500 to 525 degrees Cent. (930-980 degrees Fahr.). The metallographic structure of Steel IV is shown in Fig. 5. This probably is materially different from the structure that would illustrate Steel VII which might be more comparable to that of Fig. 9 which illustrates his Steel VIII. The structure shown in Fig. 5 is, however, quite similar to that obtained in the Watertown steels. That is, there is a fairly uniform distribution of relatively small particles of massive carbide scattered through the body of the polyhedral grains in a matrix of fine textured martensite that was found to be difficult to etch. Our Fig. 1 illustrates this carbide distribution. This represents a Watertown Arsenal molybdenum steel etched lightly with 2 per cent alcoholic nitric acid to develop grain boundaries followed by an etch in sodium picrate to color the carbides. The magnification of the original was × 1000. Our Fig. 2 shows another

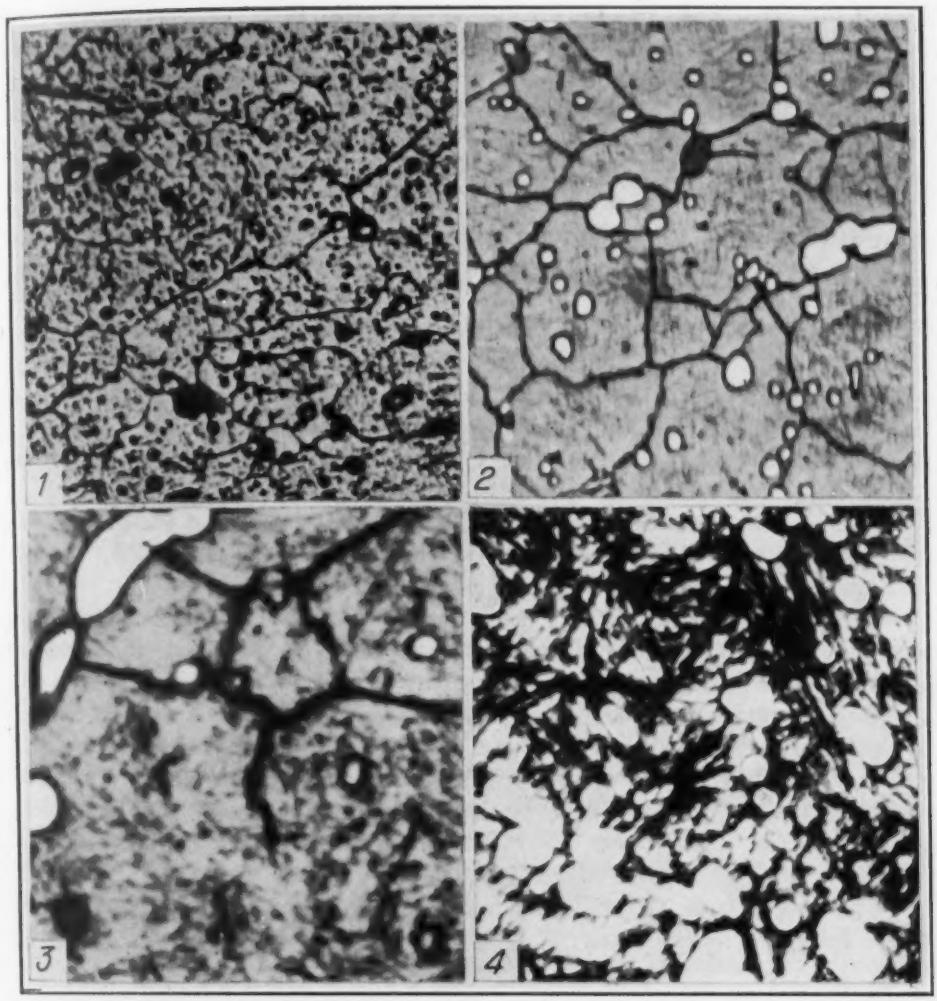


Fig. 1—Photomicrograph of Molybdenum High Speed Steel. Sodium Picrate Etch. Carbides Colored Black. × 1000.

Fig. 2—Photomicrograph of Molybdenum High Speed Steel. Nitric Acid Etch. Carbides Distributed in Fine-Textured Martensite. Note Persisting Austenitic Grain Boundaries. × 1000.

Fig. 3—Photomicrograph of Molybdenum High Speed Steel. Same as Fig. 2 Except Higher Magnification. Note Martensitic Nature of Grains. × 3350.

Fig. 4—Photomicrograph of Tungsten High Speed Steel. Nitric Acid Etch. Note Martensitic Nature of Background. No Strongly Pronounced Austenitic Boundaries. Martensite Etches with Relative Ease. × 2350.

Watertown steel that performed well in service. In this case the specimen was etched a normal time in 2 per cent nitric acid. Our Fig. 3 represents the same steel after a more prolonged etch. The very definite martensitic structure of the matrix is developed. Our Fig. 4 illustrates the structure found in a commercial tungsten steel milling cutter. It is shown to illustrate its similarity to the author's structure of Steel VIII as shown in his Fig. 9. The cutter did not perform well in service and was considered to be overhardened.

In the Watertown development good tools were judged from shop per-

formance. It was found that the character of the fracture was a very reliable guide to tool quality and was correlated with shop results. A very fine silky fracture that showed ripples in the broken surface was associated with good tool performance. These desirable fractures were not associated with maximum hardness. In practice small tools were usually somewhat harder than tungsten tools of corresponding size, Rockwell C values for molybdenum tools running from 62 to 65. For large sizes the molybdenum tools were somewhat softer than the corresponding ones of tungsten steel.

Mr. Emmons' heat treatments for maximum strength calls for quenching and tempering temperatures considerably higher than those found to be beneficial for Watertown steels. The latter developed an incorrect fracture for quenching temperatures above values between 1150 and 1200 degrees Cent. (2100-2190 degrees Fahr.), the exact hardening temperature depending on the carbon content. Even at these lower temperatures the steel could be held at heat only from one to three minutes. The tool quality was also quite sensitive to the tempering treatment. That is, 525 degrees Cent. (980 degrees Fahr.) was regarded as a maximum possible draw. The influence of soaking time at draw temperature was found to be important. Small tools are held 3 hours and larger ones 4 to 5 hours.

While it is true that drilling tests are excellent for testing drills, and that steels that made good drills should make good cutters and lathe tools, it does not follow that steels that fail in drilling will necessarily fail in other tool forms.

Shop performance is the final test of a tool. The experience at Watertown Arsenal and at commercial plants where Watertown steels were used has shown definitely that in heavy and light cutting service with lathe and planer tools, and with milling cutters and reamers, the molybdenum tools will perform on the average equally as well as the better known tungsten tools available at the present time.

The Department recently procured a quantity of molybdenum tool steel to the following specifications:

C	Mn	Si
0.65-0.75	0.15-0.30	0.15-0.30
Cr	**Mo**	**V**
3.25-3.75	9.25-9.75	1.15-1.35

S	P
under 0.025	under 0.025

This steel is now in general use at this and other arsenals, and is giving satisfactory service, especially in turning and planing operations, and to a lesser extent in milling work.

In forging and in heating operations where the temperature exceeds 500 degrees Cent. (930 degrees Fahr.), it is necessary to protect the surface of the steel by a film of borax or by other means. Otherwise, a soft surface is obtained. In hardening, the best results have been secured by heating in salt baths. Good results have been produced in other types of furnaces with positive atmospheric control.

Present practice prescribes preheating at 1550 degrees Fahr., quenching from 2150 degrees Fahr. (1175 degrees Cent.) and drawing from 935 degrees Fahr. (500 degrees Cent.)

The tools have been found to be in general equivalent to 18 per cent tungsten tool steel. Some mechanics on rough turning gun forgings on piece work prefer molybdenum tools, others make no distinction.

Oral Discussion

A. H. d'ARCAMBAL:[2] This splendid paper will undoubtedly result in further investigations on molybdenum and molybdenum-tungsten high speed steels, finally resulting, possibly, in their somewhat greater application to the metal cutting tool industry. There are, however, some shortcomings in regard to the use of molybdenum or molybdenum-tungsten high speed steels for cutting tools.

In the first place, these steels are subject to the soft skin that we find on all molybdenum and cobalt high speed steels when hardened by the usual so-called open fire method. However, should these steels be hardened by heating in a salt bath a hard skin should be obtained.

Another objection to the types of steels covered by Mr. Emmons is the somewhat closer hardening range that must be maintained in order to get away from brittleness due to overheating. In other words, I believe they compare to the 14-4-1 type, not only in regard to the properties brought out by Mr. Emmons, but also in regard to the necessity of maintaining a closer hardening range. This, however, does not mean that these molybdenum-tungsten steels will not find general use by the trade, because practically all metal cutting tool manufacturers today employ high speed steel furnaces that are automatically controlled for temperature, resulting in maintaining the desired temperature within a few degrees.

Author's Closure

The author wishes to thank the several gentlemen who have so ably contributed to the discussion of this paper.

The work of the Watertown Arsenal as reported by Colonel Jenks and Dr. Yatsevitch is particularly interesting. A great deal of credit is due to the researches of the Arsenal under General T. C. Dickson and Captain Ritchie, and more recently continued by Colonel Jenks and Dr. Yatsevitch. This work represents the highest known development of the tungsten-free molybdenum high speed steels. It is believed that the molybdenum high speed steels reported in the paper containing about one-fourth as much tungsten as molybdenum are a definite improvement over this type. Further experiments will be necessary to determine to what extent the drilling tests can be used to predict the performance of lathe, planer and other tools. The variation between the results obtained by the Watertown Arsenal and ourselves for the most satisfactory hardening and tempering temperatures in the tungsten-free steels is believed to be readily explained by the considerable variation in the time

[2]Consulting metallurgist, Pratt and Whitney Co., Hartford, Conn.

the steel was exposed to the desired temperature. For instance the Arsenal used for hardening, a temperature of 2100 to 2190 degrees Fahr. with a soaking time of from one to three minutes. The maximum secondary strength of our Steel VII was similarly developed at two hardening temperatures as follows:

2235 degrees Fahr. held at the temperature for thirty seconds.

2200 degrees Fahr. held at the temperature for ninety seconds

It has also been noted that the tungsten-bearing steels will stand slightly higher hardening temperatures than the tungsten-free steels such as have been tried at the Arsenal.

The interesting light upon the past history of molybdenum high speed steels supplied by Dr. Mathews is greatly appreciated. In regard to the possible effect of the high chromium content upon the performance of Steel XIII, it is believed that the higher carbon content has had a more important influence than the high chromium.

The discussion by Mr. Garratt presenting the results of independent work upon tungsten-bearing molybdenum high speed steels is particularly valuable. Such confirmation of our results from an independent source is regarded as being of great importance, especially so as Mr. Garratt's work bears all the earmarks of a carefully planned and executed research program. Mr. Garratt's observations in regard to the most desirable carbon content for this type of steel are confirmed by our results. As was noted in the paper, the molybdenum high speed steels require a higher carbon content in order to produce a normal amount of carbides in the microstructure and the maximum cutting quality. This increase in the amount of carbon required seems to be about 0.10 per cent more than is usually employed in 18-4-1 steels.

The comments of Mr. d'Arcambal in regard to the practical methods of heat treatment are pertinent. It has been our experience that it is also necessary to protect the 18-4-1 type of high speed steel against oxidation while it is at high temperatures in order to prevent the formation of a soft skin or bark. The same methods of protection which were developed for the 18-4-1 type have been found satisfactory for the molybdenum-tungsten type. No difficulty has been experienced with over-heating the molybdenum-tungsten type of steels after the most desirable range of hardening temperatures was determined.

Mr. Kissock's interest in the paper is greatly appreciated.

THE HARDENING TRANSFORMATION IN MANGANESE STEELS

By H. Scott and J. G. Hoop

Abstract

The hardening transformation, Ar″, though it occurs at a comparatively low temperature, is shown to be a vital factor in the quenching of steel. The temperature at which it starts was evaluated in steels containing from 4.5 to 12.0 per cent manganese and from 0.2 to 1.0 per cent carbon under conditions which assured all the carbon being brought into and retained in solid solution.

With the data available, an equivalence relation between manganese and carbon with respect to their effects on the temperature of Ar″ was established. Carbon in solid solution was shown to have twelve times the effect of manganese within certain composition limits.

The temperature of Ar″ in iron-carbon alloys was estimated by extrapolation from the general relation established for high manganese steels. Our results agree with the best published data when Ar″ starts near 250 degrees Cent. and are probably quite close to the actual location of the hardening transformation in iron-carbon alloys cooled from above the critical range at rates above the critical cooling rate.

Introduction

EVERY steel hardened by a quench which produces martensite undergoes the hardening transformation, Ar″, at a temperature considerably below that of Ar_1. The conditions which exist during this transformation determine in a large measure the success of the treatment. Thus it has been shown[1] that an oil-hardening steel of simple shape will crack or not depending on the cooling rate through Ar″, that is, below 400 degrees Cent. (750 degrees Fahr.).

An explanation for the critical importance of the cooling rate

[1]H. Scott, "Origin of Quenching Cracks," Bureau of Standards Scientific Paper No. 513, 1925.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The authors are associated with the Research Laboratories of the Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. The senior author is a member of the society. Manuscript received June 22, 1932.

during Ar″ can be derived from Fig. 1. This illustration shows the expansion that occurs when a 1.0 per cent carbon, 4.5 per cent manganese steel which is entirely austenitic at room temperature is cooled in liquid air. It illustrates what normally occurs above

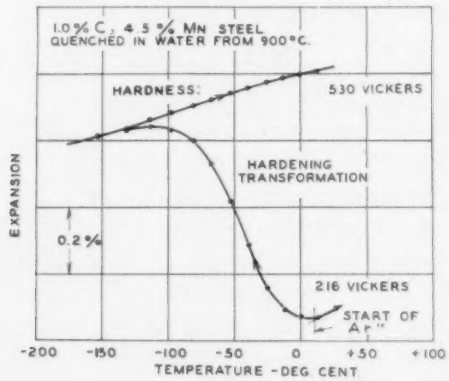


Fig. 1—Dilatation and Hardness Change During Cooling of an Austenitic Steel in Liquid Air.

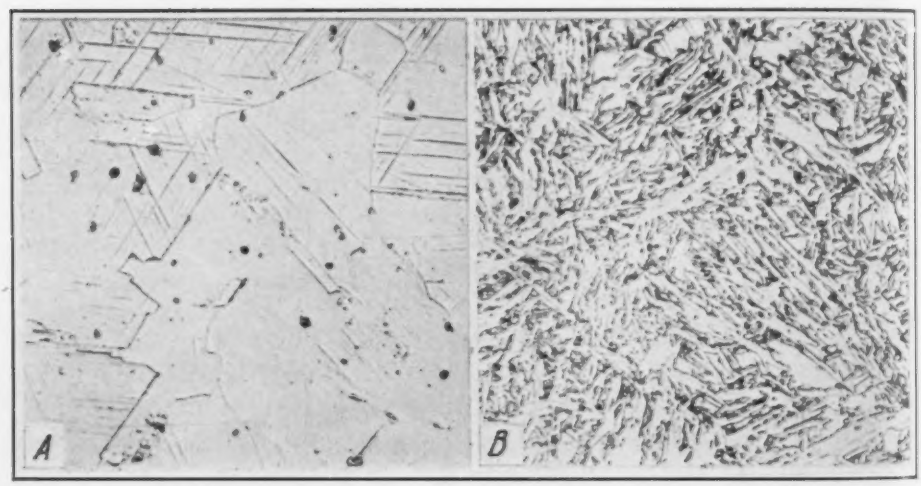


Fig. 2—Microstructure of a 1.0 Per Cent Carbon, 4.5 Per Cent Manganese Steel Quenched From 900 Degrees Cent. (A) As-quenched and (B) After Cooling in Liquid Air. × 500.

room temperature and is fully comparable with the phenomena accompanying the hardening of conventional steels. The steel in question increases in volume by more than 2 per cent and its hardness increases from 216 to 530 with the change in microstructure shown in Fig. 2.

The generation of residual stresses having magnitudes sufficient

to crack conventional steels can be explained simply, but not rigorously, as follows: During quenching the hardening transformation occurs at a temperature where the rate of cooling is still so high that a considerable temperature gradient exists in the steel. Consequently the surface hardens before the core transforms. As the core transforms, it increases in volume pressing outward on the surface layers which consequently are placed under tensional stress. Hardened and untempered tool steel is prone to crack under extreme tensional stresses which develop in outer fibers as the result of quenching. Stress of the same magnitude would be of little concern if compressional.

Both the magnitude and the direction of the residual stresses are determined by the cooling rate during the hardening transformation. Hence the cooling rate in the temperature range of the hardening transformation is a vital factor in the quenching of steel.

Further testimony as to the importance of this transformation is furnished by the continuous succession of papers on the subject starting with Le Chatelier's in 1904, see footnote references (2) to (11). Le Chatelier found that the Ar_1 transformation did not occur when plain carbon steels were cooled rapidly enough to produce complete martensitization. He recognized that some transformation must have occurred, but was unable to locate it. In 1917 both Dejean[4] and Chevenard[5] working with alloy steels established the existence of a transformation associated with martensite formation at a much lower temperature than Ar_1. Chevenard[6] and Portevin and Garvin located the same phenomena in carbon steels in 1919. It is with this transformation that the present paper is concerned.

Chevenard introduced the symbol Ar″ for the hardening transformation and Ar′ for the high temperature transformation. We know that the product of Ar′ is pearlite or an analogous constituent

[2]H. Le Chatelier, "Etudes Sur La Trempe Des Aciers," *Revue de Metallurgie*, Vol. 1, 1904, p. 473.

[3]C. Benedicks, "Experimental Researches on the Cooling Power of Liquids," *Journal*, Iron and Steel Institute, Vol. 78, 1908, p. 153.

[4]M. P. Dejean, "Les Points Critiques de Refroidissement des Aciers Auto-Trempants," *Revue de Metallurgie*, Vol. 14, 1917, p. 641.

[5]P. Chevenard, "Dilatometer Differential Enregistreur," *Revue de Metallurgie*, Vol. 14, 1917, p. 610.

[6]P. Chevenard, "Mecanisms de la Trempe des Aciers au Carbone, *Revue de Metallurgie*, Vol. 16, 1919, p. 17.

throughout the whole range of rates over which it occurs so Ar′ and Ar_1 may properly be considered as basically the same transformation. Increasing the cooling rate lowers the temperature of Ar_1 somewhat but chiefly causes this transformation to diminish in intensity and finally to disappear entirely when the "critical cooling rate" is reached. At this and higher cooling rates the steel is completely hardened, that is, the end product is martensite and Ar″ is the only transformation involved. Ar″ is of course the Ar_3 transformation of carbon-free iron alloys being continuous with Ar_3 as carbon is added. This special symbol for Ar_3 in alloys containing carbon in excess of the minimum solid solubility limit is justified by the fact that its temperature is a function of the amount of carbon in solid solution. Ar″ should therefore be taken to imply conditions of supersaturation with respect to carbon.

The hardening transformation is most amenable to experimental study in alloy steels because many of the common alloying elements lower the critical cooling rate greatly. It may seem preferable to begin the study of alloy steels with consideration of plain carbon steels. That is not the case, however, for little of the data now available on Ar″ in plain carbon steels can be accepted as accurate. The inherent experimental difficulties of observing transformations at extremely rapid cooling rates present an exceptionally severe obstacle to the collection of reliable data. It is therefore advantageous to work from the high alloy content field where precise information can be obtained towards the low alloy content field as an ultimate goal.

Of the alloying elements worthy of study, manganese is out-

[7]A. M. Portevin and M. Garvin, "Experimental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels," *Journal*, Iron and Steel Institute, Vol. 99, 1919, p. 469.

[8]K. Honda, "On the Nature of the A_1 Transformation and a Theory of Quenching," *Journal*, Iron and Steel Institute, Vol. 100, 1919, p. 417.

[9]H. Hanemann and A. Schrader, "On Martensite," TRANSACTIONS, American Society for Steel Treating, Vol. 9, 1926, p. 169.

[10]F. Wever and N. Engel, "Ueber den Einfluss der Abkühlunggeschwindigkeit auf die Temperatur der Umwandlungen, das Gefüge und den Feinbau der Eisen-Kohlenstoff Legierungen," Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung, Vol. 12, 1930, p. 93.

[11]H. Esser and W. Eilender, "Ueber die Stählhartung," *Archiv. fur das Eisenhuttenwesen*, Vol. 4, 1930, p. 113.

[12]E. S. Davenport and E. C. Bain, "Transformation of Austenite at Constant Subcritical Temperatures," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, p. 117.

standing because of its wide use in steel. A series of manganese steels containing from 4.5 to 12.5 per cent manganese and 0.2 to 1.0 per cent carbon were available for study. They had been prepared by melting 18-pound charges in magnesia crucibles in an induction furnace, casting in 2-inch square molds and forging to ⅜ inch diameter rods. Dilatation was selected as a criterion of transformation for it can be most conveniently measured and is exceptionally sensitive to phase change. Specimens ¼ inch in diameter and 2 or 4 inches long were used. The differential linear expansion with respect to fused silica was observed as previously described.[13]

Effects of Cooling Rate

The most sharply defined and significant characteristic of the hardening transformation is the temperature at which it starts. Accordingly one objective of this work was to evaluate its starting tem-

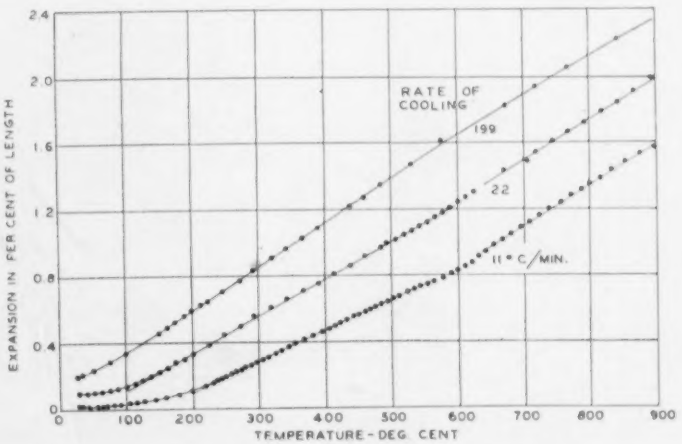


Fig. 3—Expansion Curves of 1.0 Per Cent Carbon, 4.5 Per Cent Manganese Steel Taken During Cooling from 900 to 25 Degrees Cent. at Different Rates.

perature as a function of manganese and carbon content. In order to do that unambiguously, two conditions must be met. They are: (1) the initial temperature before the determination must be such that the gamma phase alone exists and (2) the cooling rate from that temperature must be such as to retain the single phase condition until the start of the transformation. If these conditions are not met, some of the carbon may not be in solid solution at the start of Ar″ and hence that transformation will be higher than otherwise by an

[13]See foot note on page 7.

indeterminate amount for only carbon in solid solution contributes to the lowering of Ar″.

To obtain the homogeneous solid solution is simply a matter of temperature. Retention of the solid solution by fast cooling, however, requires some attention because slow cooling is favorable to accuracy of observation. Using a 4.5 per cent manganese and 1.0 per cent carbon steel, a minimum rate was found for it which was suitable for the other alloys because, being higher in manganese, they

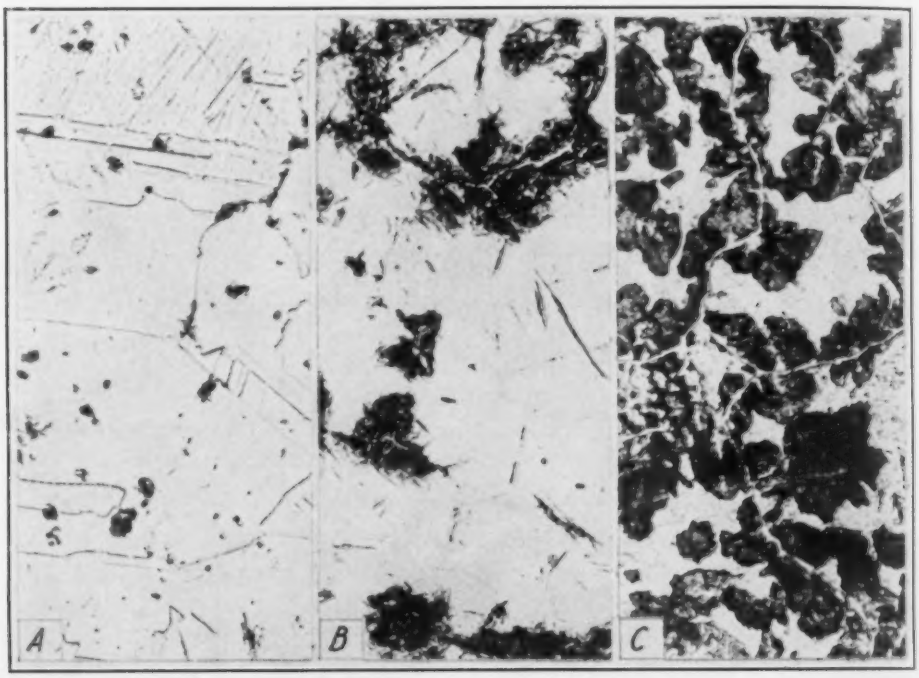


Fig. 4—Microstructure of 1.0 Per Cent Carbon, 4.5 Per Cent Manganese Steel After Cooling from 900 Degrees Cent. at Different Rates. Cooling Rate at 600 Degrees Cent.: (A) 200 Degrees Cent. Per Minute, (B) 22 Degrees Cent. Per Minute, (C) 10 Degrees Cent. Per Minute. × 500.

have a lower critical cooling rate. When that alloy was cooled in air while mounted in the silica tube of the dilatometer, the mean rate of cooling over the temperature range 700 to 500 degrees Cent. (1290-930 degrees Fahr.) was 199 degrees Cent. (358 degrees Fahr.) per minute. From the work of Davenport and Bain[12] this is the region of maximum reaction rate and consequently that where the cooling rate is most important. Above or below that temperature range considerably slower cooling rates would be required to cause precipitation of carbide, the factor most likely to give discordant results.

The expansion curve during cooling from 900 to 25 degrees Cent., Fig. 3, showed no recognizable discontinuity corresponding to Ar_1. Nevertheless a few fine-grained dark areas in the austenite matrix, Fig. 4A, indicate that Ar_1 had occurred, but that a very small volume was involved. The cooling rate of 200 degrees Cent. (360 degrees Fahr.) per minute is therefore close to the critical value. Moreover it is sufficiently slow to permit making reliable expansion-temperature observations during Ar″ at which time the cooling rate is considerably slower. All the carbon was retained in solution also since the starting temperature of Ar″ is practically identical with that following water quenching, compare Fig. 1 and Fig 6. Accordingly air cooling was adopted for specimens in which Ar″ occurred above room temperature; otherwise the specimens were quenched in water. The cooling rate during Ar″, of course, varied with its temperature. Its effect however is inappreciable because Ar″ starts in all the alloys at temperatures where the rate of carbide precipitation from an austenite matrix is extremely slow. In the absence of carbide precipitation, Ar_3 and hence Ar″ is independent of cooling rate.[13, 14]

Cooling at rates slower than the critical value brought out some points of incidental interest. The expansion curves taken at such rates, 22 and 11 degrees Cent. per minute of Fig. 3, show a small discontinuity in the region of 600 degrees Cent. (1110 degrees Fahr.). Coincidentally there is a considerable quantity (over 50 per cent for the slowest rate) of a dark constituent in the microstructure, Fig. 4B and 4C, which appears to be nodular troostite. The anomaly at 600 degrees Cent. (1110 degrees Fahr.) must therefore be identified as Ar_1. The fact that so little net expansion occurs may be attributed to the opposing effects of carbide precipitation and formation of alpha iron. In fact the change starts with a contraction evidently due to separation of carbide which forms a network associated with the dark areas of Fig. 4B and 4C. The subsequent expansion accompanies formation of the dark areas.

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[13]H. Scott, "Transformational Characteristics of Iron-Manganese Alloys," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1931, p. 28.

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[14]F. M. Walters, Jr. and M. Gensamer, "A Dilatometric Study of Iron-Manganese Binary Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 608.

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[15]H. Scott, "Dimensional Changes Accompanying the Phenomena of Tempering and Aging Tool Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 9, 1926, p. 277.

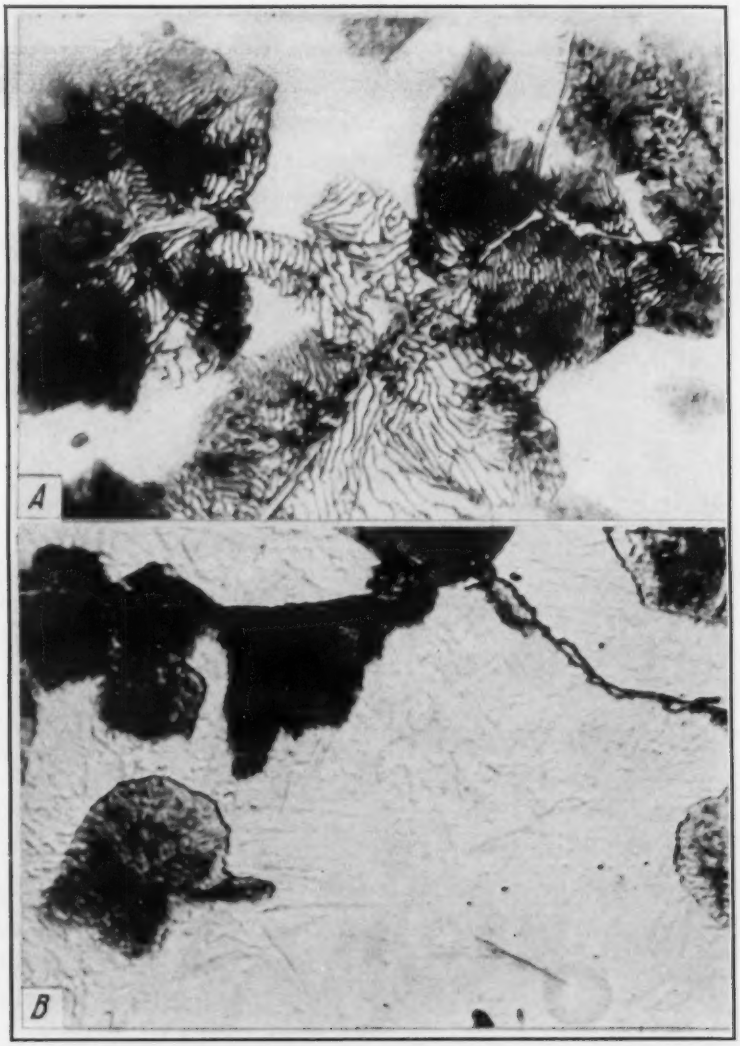


Fig. 5—Microstructure of 1.0 Per Cent Carbon, 4.5 Per Cent Manganese Steel Cooled from 900 Degrees Cent. at 10 Degrees Cent. Per Minute. (A) Pearlite in an Austenite Matrix; (B) Incipient Martensite Formation Around the Edges of a Large Austenite Grain. × 2000.

Lucas[16] and Davenport and Bain[12] have succeeded in resolving the structure of the constituent which forms at Ar_1 when martensite is also an end product and have shown that it is essentially pearlite. Further evidence to that effect is furnished by Fig. 5A. Evidently this constituent should be identified as pearlite rather than troostite because the inference may arise that its mechanical properties are

[16]F. F. Lucas, "Structure and Nature of Troostite," Bell System Technical Journal, Vol. 9, 1930, p. 101.

equal to those of tempered martensite, and that is certainly contrary to fact.

A very pronounced diminution in the slope of the expansion curves below 200 degrees Cent. (390 degrees Fahr.) is noticed as the cooling rate decreases. This indicates that in certain areas Ar″ starts between 200 degrees Cent. (390 degrees Fahr.) and zero.

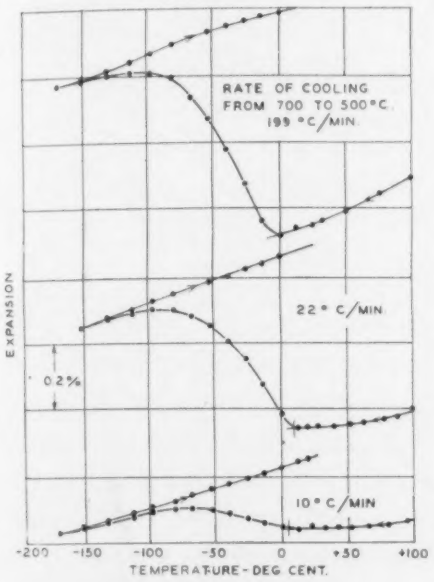


Fig. 6—Hardening Transformation in 1.0 Per Cent Carbon, 4.5 Per Cent Manganese Alloy After Cooling from 900 Degrees Cent. at Different Rates.

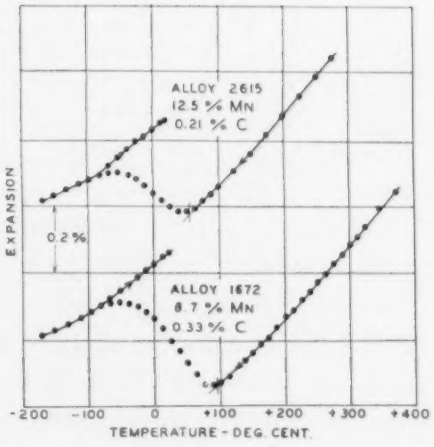


Fig. 7 — Hardening Transformation During Cooling from 900 Degrees Cent. in Air, 9 and 12 Per Cent Manganese Steels.

Nevertheless much austenite remains untransformed at room temperature since the major transformation still starts sharply and at the same temperature on cooling in liquid air, Fig. 6, and its magnitude is commensurate with the proportion of white area in Fig. 4. In conformity with this observation we find that large grains of austenite as cooled at 11 degrees Cent. per minute to room temperature show evidence of partial transformation in the vicinity of the dark constituent, Fig. 5B. This appears to be the result of carbide separation at the grain boundaries and consequent impoverishment of the adjacent matrix.

Composition Relations

Given the two composition variables, manganese and carbon, the statement of their effects on Ar″ could be greatly simplified by the

Table I

Temperature of Ar″ in Fe-Mn-C Alloys Cooled so as to Retain all Carbon in Solid Solution

Alloy	Composition %Mn	%C	%Si	%Mn + 12 (%C)	Start of Ar″	Max. Temp.	Cooling Medium	Cooling Rate
	Cooling Rate Variable							
2616	12.37	0.34	0.12	16.5	+5°C.	900°C.	Water	
2616	12.37	0.34	0.12	16.5	15	900°C.	Air	
2770	4.50	0.99	0.16	16.4	0	900°C.	Air	199°C./min.
2770	4.50	0.99	0.16	16.4	10	900°C.	Furnace	22°C./min.
2770	4.50	0.99	0.16	16.4	5	900°C.	Furnace	10°C./min.
	12% Mn, C Variable							
2615	12.49	0.21	0.12	15.0	55°C.	900°C.	Air	
2616	12.37	0.34	0.12	16.5	+5	900°C.	Water	
2617	12.16	0.53	0.10	18.5	−60	900°C.		
	4-9% Mn, C Variable							
2773	4.84	0.51	0.10	11.0	150°C.	900°C.	Air	
2772	6.78	0.43	0.12	11.9	120	900°C.	Air	
1672	8.68	0.33	....	12.6	95	900°C.	Air	
2613	7.38	0.70	0.04	15.8	0	800°C.	Water	
2770	4.50	0.99	0.16	16.4	+10	900°C.	Water	

establishment of an equivalence between manganese and carbon. Such a relation between nickel, manganese and carbon with respect to Ar_3 has alrady been demonstrated for a limited range of compositions.[13] The carbon content of those alloys, however, was low and probably less than the minimum solid solubility limit so the equivalence ratio cannot be expected to hold at high carbon contents. It is therefore desirable to investigate the possibility of a similar relation in high carbon manganese steels.

The temperatures at which Ar″ starts were taken from the curves already given and from Figs. 7, 8, 9 and 10 and are given in Table I together with compositions. Values for Ar_3 in low carbon iron-manganese alloys taken from recent publications.[13, 14] have also been used to provide data on low carbon contents.

An equivalence ratio is readily found if a pair of steels having the same Ar″ but different carbon contents are available. Three such pairs are available in the case of alloys No. 2613, No. 2616 and No. 2770, all of which show Ar″ starting between 0 and 5 degrees Cent. The equivalence ratio for any pair is the difference in manganese contents divided by the difference in carbon contents. For the three possible combinations of the alloys mentioned in pairs, the mean of this ratio is 11.9. That is to say, carbon has nearly twelve times the effect of manganese in lowering Ar″ when this transformation starts close to 0 degrees Cent.

No such fortunate combination of compositions was available

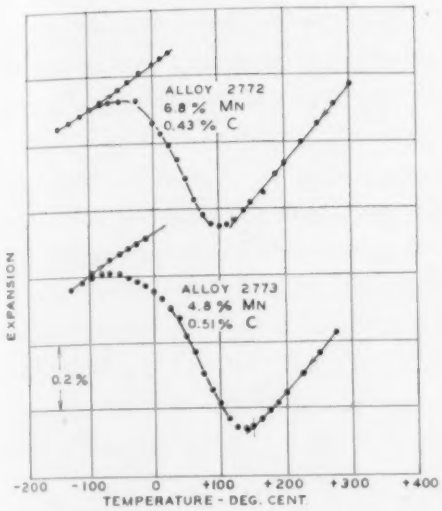


Fig. 8 — Hardening Transformation During Cooling in Air from 900 Degrees Cent. of 5 and 7 Per Cent Manganese Steels.

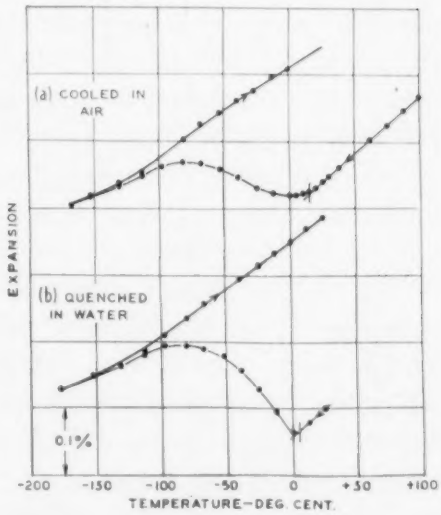


Fig. 9—Hardening Transformation in 0.34 Per Cent Carbon, 12.4 Per Cent Manganese Steel after Cooling in Air, (A) and Quenching in Water (B).

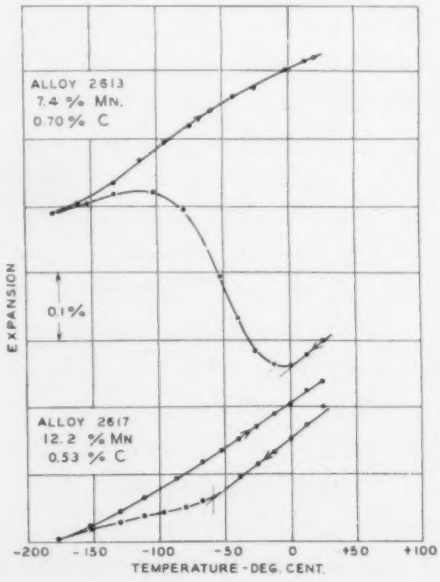


Fig. 10 — Hardening Transformation During Cooling in Liquid Air, 7 and 12 Per Cent Manganese Steels.

for other Ar″ temperatures. One may still interpolate, however, with the curve for low carbon alloys at higher temperatures to find a low carbon alloy having the same Ar″ as a high carbon alloy. Alloys No. 1672, No. 2772 and No. 2773 so compared with low carbon alloys gave a mean value of the equivalence ratio of 12.3 for tem-

peratures of Ar″ between 100 and 150 degrees Cent. Accordingly the value of 12 is taken as the round number best representing the equivalence of carbon to manganese when Ar″ starts between 0 and 150 degrees Cent.

The advantage of using this ratio may now be shown by plotting the temperature of Ar″ against the equivalent manganese content, that is, the manganese content plus 12 times the carbon content, as in Fig. 11. So plotted, the values for all the alloys line up very well on a smooth curve in spite of the fact that the range of carbon content extends from 0.02 to 1.0 per cent. Hence to find the start of Ar″ in a carbon-manganese steel of known composition with all the carbon in solid solution one need only calculate the equivalent manganese content and resort to the curve.

The curve of Fig. 11 is certainly applicable for a wider range of Ar″ temperatures than that used for determination of the equivalence ratio. Nevertheless there are certain precautions which must be observed in its use. For one thing the curve below 200 degrees Cent. (390 degrees Fahr.) is not accurate for carbon contents less than 0.2 per cent. A new phase, epsilon, appears in the range of compositions involved (high manganese content) to complicate matters. Above 200 degrees Cent. (390 degrees Fahr.) there is no restriction on the minimum carbon content, but no information is available on the upper limiting carbon content. It is highly probable, however, that the range of carbon contents for which the curve holds at the lower temperatures applies also at considerably higher temperatures. In fact some values on low manganese content steels presented in the next section conform very well with this relation. There remains, however, need for further work in the range 200 to 500 degrees Cent. (390 to 930 degrees Fahr.) within which fall many of the steels commonly subjected to hardening.

One application of the equivalence relation is to the determination of the limiting contents of manganese and carbon required to retain 100 per cent austenite at a particular temperature when properly cooled. For room temperature one may take from Fig. 11 the relation:

$$\%\ \mathrm{Mn} + 12\ (\%\ \mathrm{C}) = 16.0$$

This equation signifies that when restricted to carbon contents over 0.2 per cent, the equivalent manganese content must exceed 16 per cent in order to retain gamma iron at room temperature. In other

words it defines a boundary line on the ternary diagram for constitution at room temperature. Another application for the equivalence relation is to estimate the location of Ar″ in low manganese steels, which matter is the subject of the following section.

Low Manganese Steels

The experimental determination of Ar″ in low alloy content steels presents unusual difficulties because of the extremely high cooling rates required to produce martensite. Most of the experimental work in this field has been confined to determination of time-temperature curves at the center of conveniently sized cylinders during quenching in water. The temperature gradients thus produced were so high as to preclude the possibility of accurately locating the start of Ar″. Chevenard, however, ingeniously eliminated the difficulty of temperature gradients by cooling fine wire specimens in non-oxidizing gases. The transformation was clearly revealed by the dilatation of the wire so that the time at which the transformation started could be accurately determined. Unfortunately the corresponding temperature was not accurately determined. It was measured by the contraction of a comparison wire presumed to cool at the same rate as the specimen.

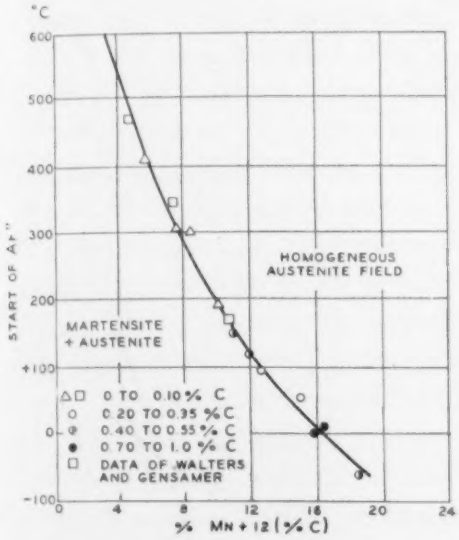


Fig. 11—Start of Hardening Transformation, Ar″, Plotted Against Equivalent Manganese Content.

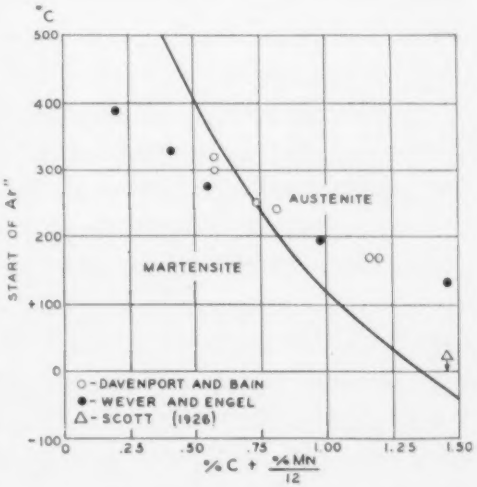


Fig. 12—Start of Hardening Transformation Plotted Against Equivalent Carbon Content (solid line). The Individual Observations Represent Carbon Steels Containing Less than 1.0 Per Cent Manganese.

Recently the same method of cooling has been used by Wever and Engel[10] and the temperature measured by welding fine thermocouple wires to the specimen and observing their electromotive force with an oscillograph. The transformation was recognized by the inflection on a time-cooling rate curve obtained by connecting a second thermocouple with the oscillograph through a transformer. They collected considerable data which deserves attention here. Davenport and Bain[12] have also determined Ar″ in a simple and effective though indirect manner. Thin strips heated for quenching as held in a dilatometer were plunged into a salt bath maintained at a predetermined temperature. The dilatation-time curves obtained at several temperatures permitted construction of curves showing degree of completion of the transformations as a function of temperature and time. From these curves the temperatures at which Ar″ starts in their several steels were taken for use here.

The equivalence relation of Fig. 11 permits estimation of the location of Ar″ in iron-carbon alloys simply by extrapolation to zero manganese content. As it is more convenient now to consider carbon as the major element, the curve of Fig. 11 is replotted in Fig. 12 against equivalent carbon content. Being obtained by extrapolation, this curve lacks the certainty of the former and for this reason comparison with the direct determinations cited is desirable.

The observations of the authors mentioned are plotted in Fig. 12 to the scale of the extrapolated curve. It is at once evident that their values are in fair agreement for alloys giving Ar″ temperatures near 250 degrees Cent. (480 degrees Fahr.), but much higher than the curve at carbon contents above the eutectoid composition. This discrepancy is obviously due to incomplete solution of carbon and is verified by an observation made on a 1.37 per cent carbon steel.[13] That steel was completely austenitic at room temperature as quenched in water from 1100 degrees Cent. (2010 degrees Fahr.) so a point is plotted for it to represent Ar″ starting below 25 degrees Cent. As this point is very much closer to the extrapolated curve than the others, the former curve assuredly represents the temperature of Ar″ in hypereutectoid steels when all the carbon is in solid solution much better than do the plotted observations.

At carbon contents below the eutectoid, the data of Bain and Davenport agree substantially with the extrapolated curve, but unfortunately do not extend to carbon contents low enough to permit a satisfactory comparison. The values of Wever and Engel extend

to sufficiently low carbon contents, but they then fall below the curve as do the comparable observations of Davenport and Bain. It is quite probable, however, that their low carbon points are on the low side of the exact relation because of the more rapid cooling necessary to the development of Ar″ when it occurs at these higher temperatures. Temperature gradients between thermocouple and specimen, the chief source of error in their test method, would then tend to give low values for Ar″ and would be greater the faster the cooling. Knowing also that Ar_3 falls above 900 degrees Cent. (1650 degrees Fahr.) in pure iron one would expect that with diminishing carbon content Ar″ would approach zero carbon content more smoothly than is required by the plotted points of Wever and Engel's observations.

So far attention has been called chiefly to the discrepancies between the three independent determinations of Ar″ in carbon steels. The fact remains, however, that all three determinations are in good agreement on the start of Ar″ when it falls in the neighborhood of 250 degrees Cent. (480 degrees Fahr.). It also seems quite certain that the curve of Fig. 12 below that temperature is close to the facts when the carbon has been completely dissolved. The uncertainties lie chiefly on the region below 0.60 per cent equivalent carbon content and further work is required in that field. It appears that the experimental methods of Bain and Davenport appropriately modified and that of the authors offer a better means for satisfactorily determining the location of the hardening transformation in carbon steels than any heretofore proposed.

Summary and Conclusions

The hardening transformation, Ar″, at which martensite forms, starts at a comparatively low temperature in commonly used high tensile strength steels. The cooling rate during its progress nevertheless determines the magnitude and direction of residual stresses which are the primary cause of cracking. Despite the practical importance of Ar″, its most sharply defined characteristic, temperature of start, is known with certainty for very few steels. The extremely high cooling rates required to produce martensite in carbon steels present a serious obstacle to accurate evaluation of that characteristic. Advantage was taken of the slower cooling rates which are permissible in manganese steels to obtain reliable values of the incidence temperature of Ar″ in them as an advantageous approach to its evaluation in conventional steels.

Upon cooling a 1.0 per cent carbon, 4.5 per cent manganese steel at various rates from above the solvus, it was found that the critical cooling rate of this steel is close to 200 degrees Cent. (360 degrees Fahr.) per minute. That or faster cooling rates retained all the carbide in solid solution and repressed Ar_1. An entirely austenitic microstructure was then obtained at room temperature which transformed to martensite on cooling in liquid air, Ar″ starting at 0 degrees Cent. Cooling this steel at slower rates produced the constituent forming at Ar_1 and often identified as nodular troostite but which has a well developed pearlitic structure as noted by Lucas, Davenport and Bain. The designation troostite is improper as it implies properties of tempered martensite not attainable in pearlite.

From the data here obtained and otherwise available it was shown that carbon in solid solution is twelve times as effective as manganese in lowering Ar″. Taking advantage of this relation, the temperature of Ar″ was plotted against the equivalent manganese content, that is, the manganese content plus twelve times the carbon content. All the points fell close to a smooth curve although the carbon contents ranged from 0.02 to 1.0 per cent. This curve shows that at room temperature manganese-carbon steels are completely austenitic when the equivalent manganese content is 16 per cent provided that the carbon content is between 0.2 and 1.0 per cent and is in solid solution. Under similar limitations the temperature of Ar″ in a manganese steel can be estimated from its carbon and manganese contents when Ar″ starts between —50 and 300 degrees Cent.

Extrapolating from the data on manganese steels, the curve for Ar″ versus carbon content of manganese-free steels was obtained. This curve agrees with the best published data on carbon steels when Ar″ starts in the neighborhood of 250 degrees Cent. (480 degrees Fahr.). At lower temperatures the older observations are high presumably due to incomplete solution of the carbon. In spite of discrepancy with one observer at higher temperatures it is believed that the derived Ar″-equivalent carbon curve here proposed for carbon steels is close to the truth.

Acknowledgments

During this investigation commendable service was rendered by Miss M. Ferguson in the preparation of photomicrographs and by Mr. J. Kelly in the preparation of alloys. Accurate chemical analyses made by Mr. R. H. Wynne made possible the establishment of the equivalence relation.

DISCUSSION

Written Discussion: By E. C. Bain and E. S. Davenport, U. S. Steel Corporation Research Laboratories, Kearny, N. J.

At the outset of this paper the authors set forth an extremely clear conception of the nature of the transformation of austenite and it is particularly pleasant to read such a lucid discussion of the distinction between the reaction in the Ar′ region to pearlite and the reaction at lower temperatures in the Ar″ to martensite.

We are inclined to feel less certain than the authors that there is a single temperature for any steel which may properly bear the designation of an Ar″ *point*. It is our impression that if one quenches a small piece of steel to a temperature safely below that at which any fine pearlite can form, avoiding thereby the possibility of any Ar′ reaction, further cooling can only result in a reaction properly designated as Ar″. Now the precise temperature at which transformation then begins in a steel so treated is entirely a function of the final cooling rate and the transformation may begin at any temperature over a fairly wide range. The product of the transformation, brought about in the manner just described, is certainly not the nodular fine-pearlite constituent found associated with martensite in a steel quenched in the conventional manner but at a rate less than the critical quenching speed, nor is it pure martensite unless the transformation is forced down to a temperature below about 100 degrees Cent. (212 degrees Fahr.). Notwithstanding, these products form a completely continuous series with no abrupt change in any characteristics which would warrant the assignment of a single definite critical point. This continuity is particularly marked in steels containing less than about 0.50 per cent carbon and comparatively small proportions of alloying elements. Nevertheless, the authors make out a very strong case for considering Ar″ to be that temperature range wherein austenite transforms only in a matter of hours at the upper limit and in a matter of seconds at the lower limit. It is our belief that the temperature found experimentally for Ar″ will vary over this range depending upon the rate of cooling in the approximate range 450 to 150 degrees Cent. (842 to 302 degrees Fahr.).

In the chart of the authors' Fig. 12 it will be seen that the points of Wever and Engel are not greatly different from the points which Messrs. Scott and Hoop have estimated from our own transformation rate studies, but that these points differ considerably from the curve drawn in conformance with the manganese-carbon equivalence. The authors account for this discrepancy, in part, by an assumption that the carbide was not wholly dissolved in the studies of the investigators cited. As far as our own studies are concerned, we may say with assurance that the specimens were all examined microscopically to make certain that no carbide remained undissolved, and in addition there was at least fair evidence that the austenite was homogeneous. We are persuaded that this explanation of the discrepancy is not entirely valid.

In connection with the authors' reference to the mechanical properties of tempered martensite, we should like to call attention to the dissimilarity in properties between a martensite tempered in the conventional manner after quenching to room temperature and the product of the decomposition of austen-

ite which transformed well below Ar′ but above the Ar″ temperature as designated by Messrs. Scott and Hoop. Even though these two materials possess precisely the same Rockwell hardness, their microstructure and dynamic properties may be quite different. It has seemed to us that the time is not far off when metallurgists will find it convenient, if not absolutely necessary, to agree more precisely on the names of these structures intermediate in properties between martensite and fine-pearlite.

Written Discussion: By John F. Eckel, research fellow, Carnegie Institute of Technology, Pittsburgh.

I have greatly enjoyed reading this paper and I wish to congratulate the authors. There is, however, one point which I believe should be more fully

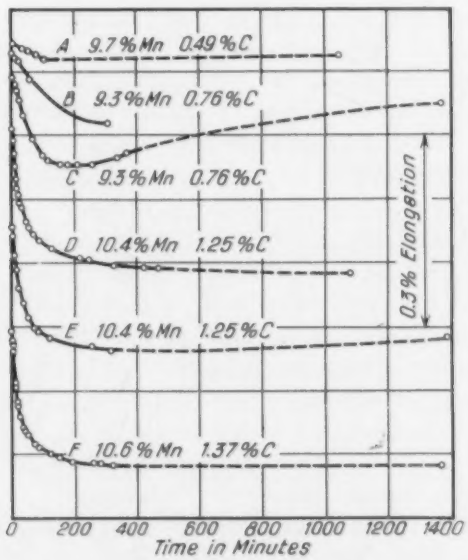


Fig. 1—Curves Showing the Length Changes Occurring During Soaks of Homogenized Specimens of the Hypereutectoid Alloys. All Curves for Soaks at 500 Degrees Cent.

emphasized at the present time and that is the possible influence which the carbon content, and consequently carbides, may exert upon the formation of pearlitic or troostitic structures, or, as the authors choose to put it, the Ar_1 transformation. As the authors say, "It may seem preferable to begin the study of alloy steels with consideration of plain carbon steels. That is not the case, however, for little of the data now available on Ar″ in plain carbon steels can be accepted as accurate." Likewise, a still higher manganese content may serve to throw more light on the effect of carbide precipitation which they refer to as "the factor most likely to give discordant results."

In working with iron-manganese-carbon alloys containing 10 per cent manganese, I have found that the Ar_1 transformation could not be induced to occur in the hypoeutectoid alloys without severe working of the gamma phase in the temperature range just below the upper stable limit of the alpha phase. In the hypereutectoid alloys, on the other hand, the Ar_1 transformation occurs

very readily. The question then arises, what is the cause of this very different behavior between hypoeutectoid and hypereutectoid alloys of this character?

A specimen of each of the alloys investigated was quenched and then held in the dilatometer at 500 degrees Cent. (932 degrees Fahr.) for several hours in order to observe the length changes occurring during such treatment. No perceptible change occurred in the hypoeutectoid alloys, but the hypereutectoid alloys showed very definite changes, which have been plotted in Fig. 1 of this discussion as a function of time. These curves show that for each alloy the first part of the decomposition reaction produces a contraction which is to be attributed to the precipitation of carbides from the supersaturated gamma solid solution. Furthermore, the initial velocity of the reaction as determined by the initial slope of these curves appears to be a function of the carbon content.

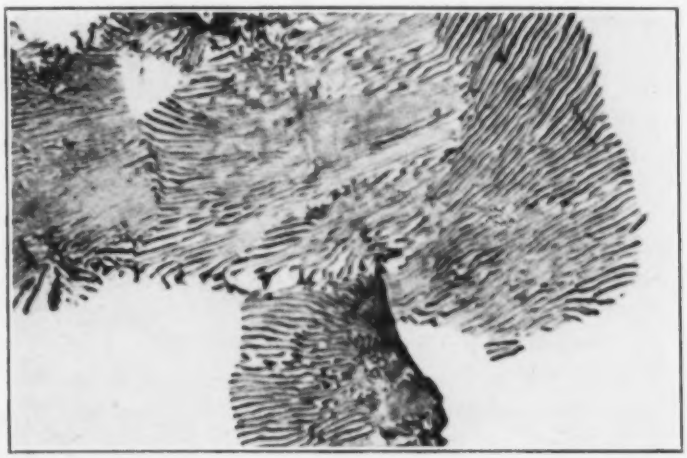


Fig. 2—Photomicrograph of a Specimen of a 0.76 Per Cent Carbon, 9.4 Per Cent Manganese Alloy. Note the Relation of the Primary Carbides to the Pearlite. Etched: Sodium Picrate. × 2000.

Later, the actual formation of a pearlitic structure manifests itself by a small expansion. When these specimens were examined microscopically, primary carbides surrounded by pearlitic structures were observed, quite similar to Figs. 4C and 5A of the authors' paper. Even specimens heat treated only two hours, and in which the predominant part of the reaction as recorded dilatometrically was the precipitation of carbides, showed large masses of pearlite, Fig. 2 (this discussion).

Since the initial velocity of this precipitation and decomposition reaction appears to depend to some extent upon the carbon content of the alloys, it is only natural to suppose that the critical rate of cooling as discussed by the authors would also depend upon the carbon content of the particular alloy in question.

The actual mechanism involved in the Ar_1 transformation of these alloys is a matter of conjecture, but the following one suggests itself after a study of the constitutional diagram. The formation of carbides rich in manganese removes both manganese and carbon from the gamma phase, so that its composition in the region immediately adjacent to the carbide soon reaches the binary

eutectoid line at a lower manganese concentration. When the binary eutectoid line has been reached, the formation of pearlite may proceed quite easily and will occur in the areas near the primary carbides before carbide precipitation has been completed.

In conclusion, I should again like to call to attention the fact that the precipitation of carbides plays an important part in the Ar_1 transformation in this type of alloy.

Written Discussion: By A. M. Portevin, Paris France.

In order to study conveniently the hardening transformation Ar″, H. Scott and J. G. Hoop were right in choosing steels containing sufficient manganese to have a low critical cooling rate.

Steels with low critical cooling speeds do, in effect, present the phenomena in "slow motion," and all the experimental difficulties of correct observation and recording of the phenomena are thus avoided. Moreover, it is with steels of low critical cooling speed that Osmond, a long time ago, first noted the doubling of the transformation on cooling and connected these two stages with the formation of troostite and martensite, thus establishing the general relationship between the microstructure and the position of the transformation point. We have called the two stages Ar′ and Ar″, as has also M. Chevenard.[1, 2]

Slow transformations lend themselves quite easily to self (automatic) recording, which is preferable to determination by points on dilatometric curves as the authors have done, because in the latter method phenomena which show as very slight variations in dilatability may pass unnoticed. An example is found in the irregularities accompanying the precipitation of cementite from austenite in tempering hypereutectoid steels, as we have shown in collaboration with M. Chevenard in our work on tempering.[3]

Similarly, in order that the structures may be conveniently observed, they must be formed at a greatly reduced speed; when one does not have at his disposal the remarkable examination methods of Dr. Francis F. Lucas, by which he obtains such excellent photomicrographs at enormous magnifications, one can use the method we have described[3] which permits the structure to grow by slackening the cooling speed sufficiently during the period the particular structure forms. One can then use ordinary magnifications to study the structures thus obtained.

It is by this means that we showed, a long time ago, that the nodular constituent forming at Ar′ and accompanying the martensite or austenite in manganese steels is pearlite in which one can recognize the radiating or fan-shaped lamellae. In his high magnifications Lucas has also found these lamellae in the nodules of troostite. Several photomicrographs are reproduced from our original paper[4] showing in particular that the nodules of troostite

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[1]A. Portevin, "Sur Les Points de Transformation Des Aciers Nickel-chrome," *Revue de Métallurgie*, Vol. XIV, p. 707, 1917.

[2]P. Chevenard et A. Portevin; "Contribution à l'étude du Revenue, Des Aciers Trempés." Congrès International des Mines et de la Métallurgie de Liège, Juin 1930.

[3]A. Portevin, C. R., 172, 1921, p. 964.

[4]A. Portevin, C. R., 165, 1917, p. 62.

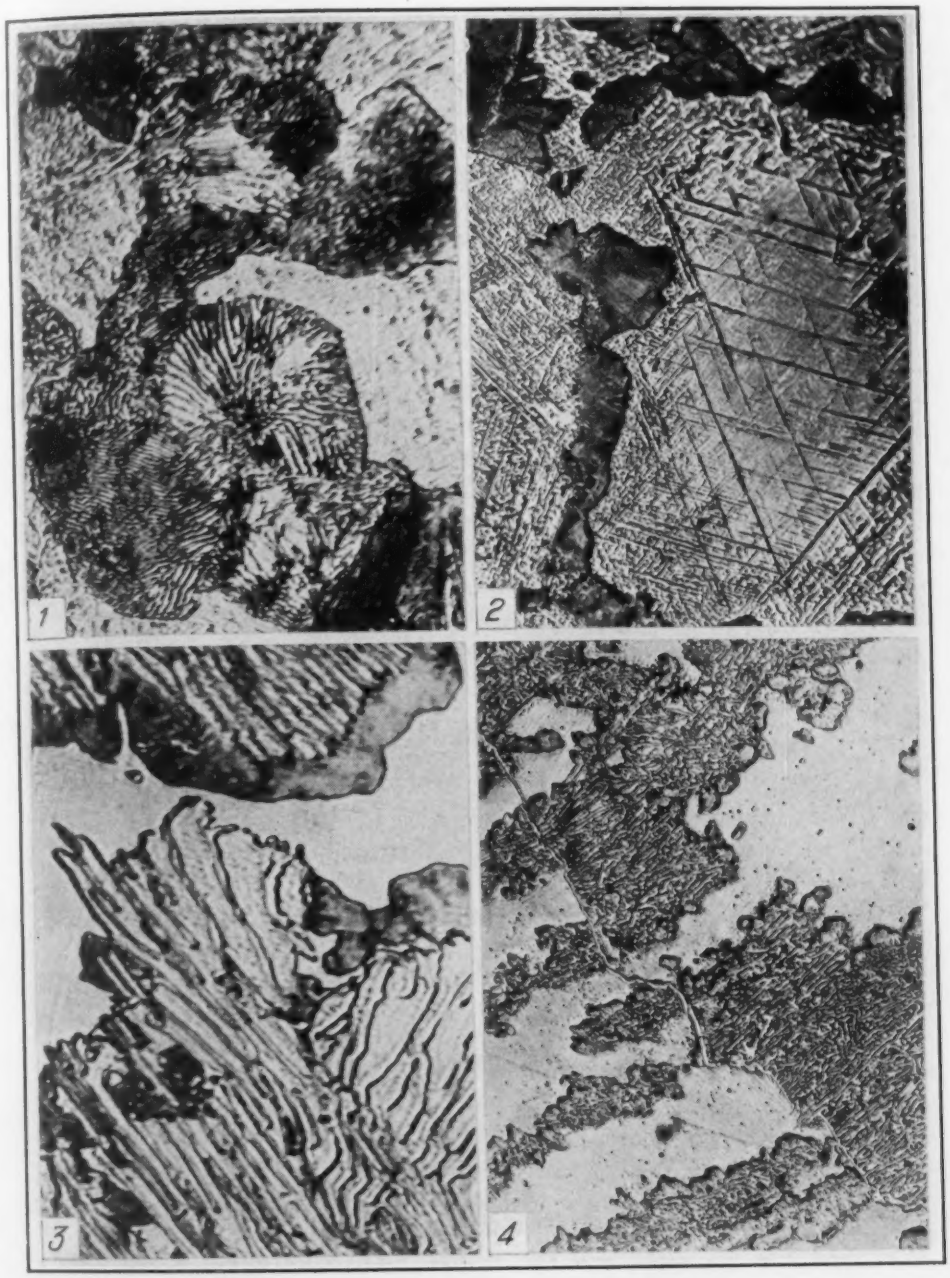


Fig. 1—Carbon 0.9 Per Cent; Manganese 7.2 Per Cent. × 1000.
Fig. 2—Carbon 0.7 Per Cent; Manganese 9.8 Per Cent. × 550.
Fig. 3—Carbon 1.00 Per Cent; Manganese 12.00 Per Cent. × 400.
Fig. 4—Carbon 1.00 Per Cent; Manganese 16.3 Per Cent. × 300.

disseminated in the austenite of manganese steel are sometimes surrounded by a boundary of martensite resulting from the Ar″ transformation due to impoverishment of the austenite in carbon following the precipitation of the

cementite (Fig. 2). The directions of this martensite are prolonged in the austenite which appears to be cleft in three orientations.

Other photomicrographs of a 0.9 per cent carbon, 10 per cent manganese steel are also attached, Fig. 3 showing the pearlite lamellae and Fig. 4 the curious dendritic appearance of the pearlite mass.

It is obvious then that by sufficiently slow cooling of an austenitic manganese steel, not only troostite but also the lamellar structure of pearlite will appear, at the same time retaining the nodular forms of the troostite or dendritic forms in which the orientation of the lamellae is in accord with the direction of the dendrites.

In this way, numerical relationships (equivalence ratios), such as those of Messrs. Scott and Hoop, relating Ar″ with the carbon and manganese content or, what amounts to the same thing, relating the microstructure and the chemical composition, are only valid in well-defined conditions of cooling.

These ratios are useful and convenient in making a quick general determination in simple cases, but they should be considered only as a first approximation; complete knowledge of the problem can only be furnished by characteristic curves as we have defined them in general and determined them for certain specific steels, with M. Chevenard,[5] by using the dilatometric method not only to find the transformation temperatures but also the amplitude of the transformations which measure quantitatively the proportion of the constituents formed.

Oral Discussion

E. C. Bain: There are several points in Mr. Scott's paper to which I would like to refer. The first is that in one of the slides he showed an arrow pointing up to about the vicinity of 600 degrees Cent. and said, "beginning of Ar double prime."

We have never found a steel that transformed to anything resembling martensite in that temperature range, such transformation always having yielded some form of pearlitic structure which could be resolved at the highest magnification. Therefore, I think that value is several hundred degrees too high for the Ar″.

Another point I would like to ask Mr. Scott more about is the alloy represented by the little triangle in his Ar″ chart. The Ar″ point for that alloy was marked to be somewhere in the vicinity of zero degrees Cent. If that be true, then that material as quenched in 1926 must now in 1932 still be wholly austenitic and absolutely nonmagnetic. Our experience with alloys of about that composition indicates they will not remain wholly austenitic.

I was much interested in what Dr. Eckel had to say about the extreme slowness with which the high manganese alloys, comparatively low in carbon, transform in the Ar″ or Ar′ region. We have observed the same thing. We do not find, however, that they never transform. It is merely that they are very slow; after hundreds of hours they do transform to pearlite. We attribute that to some such circumstance as this: When carbide forms out of high man-

[5]A. Portevin and P. Chevenard, "The Characteristic Curves of the Heat Treatment of Steels." *Journal*, Iron Steel Institute, Vol. CIV, p. 117, 1921.

ganese alloys, that carbide is very much richer in manganese than the alloy as a whole. Therefore the austenite becomes leaner in manganese, which is the outstanding element retarding transformation, and the alloy now impoverished in manganese can transform with increasing rapidity. If the carbon is low, you do not have this depletion of manganese in the austenite taking place and therefore the reaction proceeds with extreme slowness.

Does Mr. Scott mean by the Ar″ point the beginning of the transformation of austenite to martensite, or other products, or the conclusion of that change? If he means beginning, then his steel quenched in 1926, I still insist, must be wholly austenitic today. If it is not, then Ar″ is at some higher temperature than the room temperature of his storage place.

HOWARD SCOTT: We consider only the start of the transformation. Of course, there is no very definite end for the high carbon series.

E. C. BAIN: Then the piece is still austenite?

HOWARD SCOTT: If we had kept it, it should be, but this piece was used in getting certain further information. It was cooled down below room temperature and no sample was kept, but I agree that it should be austenitic.

P. H. BRACE:[1] I would like to know whether Mr. Bain has samples which have exhibited, over a period of years, the type of continued transformation suggested in his discussion. Perhaps Mr. Scott will have to prepare another sample to verify the location of the point on his diagram, whose location Mr. Bain has questioned.

E. C. BAIN: I have no very complete record, although I am thinking, with a good deal of regret, of the time I published something about a steel, containing relatively small amounts of nickel and manganese, which I thought was austenitic, but which had only been austenitic for a very short time; within a few days it was martensitic.

P. H. BRACE: With regard to magnetism and allotropy, it is my understanding that so far no definite X-ray evidence has been shown of changes in crystal lattices or system of crystallization coincident with the magnetic transformation in iron. Recently Dr. Bitter, working with Dr. Yensen in the Westinghouse Laboratories, has performed some interesting experiments in which he magnetized single crystals of iron produced when the iron was melted and allowed to cool slowly so that very large crystals were developed. When these crystals were magnetized and the surface coated with an extremely fine magnetic powder Dr. Bitter found that a definite pattern was produced by local accumulations of magnetic powder in the form of uniformly-spaced parallel straight bands across the surfaces of the crystals. The spacing of the bands was of the same order as that of slip bands that might occur in the material when cold-worked. Definite relations between the two have not as yet been demonstrated, but the experiment gives an idea of the scale of apparent aggregates responsible for ferro-magnetism in iron.

There are other cases which may be mentioned in which aggregates of molecular type are apparently the controlling factor; for example, the formation of highly magnetic alloys from completely nonmagnetic constituents. Led

[1]Manager of the metallurgical division, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

by these phenomena, physicists are coming to the thought that magnetism is determined by molecular aggregations and not by atomic properties alone and visualizing the mechanism in terms of groups of atoms which may run into hundreds of thousands in single blocks co-operating as regiments rather than functioning as individuals.

It seems to me that by defining allotropy pretty clearly we would eliminate the Curie magnetic change from the picture and that as a result some of the difficulties and confusion arising from the beta iron controversy would be cleared away. I venture to define allotropy as a spontaneous change of physical properties with temperature resulting from abrupt changes of crystal lattice type or parameter.

R. S. ARCHER:[3] It might be pointed out that medium manganese steel is getting into a ternary alloy and we might expect a range of temperature in that case which we would not expect in the purer binary series.

Author's Closure

It is very gratifying to get these pertinent comments from a variety of viewpoints. Regarding the discussion by Messrs. Bain and Davenport, it might appear that we are very much at odds. That is not so. I agree fully that the temperature of Ar″ is a function of the "final cooling rate" as they put it when that rate is comparatively slow. It has been proved to be so by them in a very clear-cut manner. The discrepancy between our views resides in the question: What is the minimum rate at which no carbide precipitation can occur?

In this connection Bain and Davenport bring up the point that rate of cooling at lower temperatures than that at which we measured it is important in determining carbide precipitation. Again we must agree. From the way the experiments were made, however, it may be seen that the rate of cooling at lower temperatures, say 450 to 150 degrees Cent., is some constant fraction of the rate actually measured. As Bain and Davenport have already shown, the rate of reaction (carbide precipitation) in that range diminishes very rapidly with temperature. In fact, it appears to diminish more rapidly than does the rate of cooling. That is why we are confident that carbide did not precipitate to any appreciable degree.

With respect to the lack of agreement between our estimation of the location of Ar″ in low manganese content steels and their more direct determinations, Messrs. Bain and Davenport point to the fact that the carbide in their steels was entirely dissolved when the steels were quenched. It does not follow, however, that all the carbide was retained in solid solution when Ar″ was reached. The microscope does not appear to be competent to detect the fine dispersion of carbide which may be present under these conditions.

Attention is quite properly called to the difference in mechanical properties between a steel as ordinarily quenched to room temperature and the same steel quenched to a temperature just above Ar″, then cooled slowly to room temperature. It is interesting to note that such a finding was anticipated by X-ray studies of quenched steel reported in TRANSACTIONS last year by N. P.

[3]Director of research, A. O. Smith Corp., Milwaukee, Wis.

Goss. He found much less grain distortion after a retarded quench than after a normal quench. This finding would be expected also from the large volume change during the hardening transformation. By slowing down the rate of formation of martensite more time is available for relaxation of the inevitable stresses that produce distortion. One should expect, therefore, that the steel cooled more slowly through Ar″ will have appreciably better mechanical properties.

After a well-considered statement of the reactions at Ar_1, Dr. Eckel calls to our attention the fact that the critical cooling rate depends on the carbon content. One might question, therefore, our assumption that the critical cooling rate determined on the steel of lowest manganese content and highest carbon content is the lowest for the group of steels studied. The effects of alloying elements, however, and particularly manganese are much more powerful than that of carbon, so the carbon content is probably of secondary importance in this respect. Also we have assured ourselves by microscopic examination that Ar_1 occurred in none of the specimens used in determining Ar″.

In his oral remarks, Mr. Bain is perhaps justified in his criticism of our extension of the curve: start of Ar″ versus equivalent manganese content, to 600 degrees Cent. when we had no data in that vicinity. It is, however, certainly representative of carbon-free alloys and the limiting carbon contents are fully stated in the figure.

With regard to the structure resulting from a steel showing Ar″ at 600 degrees Cent., it may be noted that according to our curve a steel containing 0.5 per cent manganese and 0.22 per cent carbon should transform to martensite at that temperature. Of course, a very rapid quench would be required to produce martensite in that composition, but the product of a sufficiently rapid quench would certainly have characteristics of martensite. Here again the evidence of the microscope is not necessarily conclusive and the answer may reside in how one defines martensite.

Mr. Bain suggests that high carbon austenite is not stable at room temperature. Extrapolating Davenport and Bain's curves of reaction time versus temperature to room temperature for the condition that Ar″ occurs below room temperature, the rate of reaction is seen to be extremely slow though of course finite. This is verified by experience with precision gage blocks. These blocks are made of martensitic high carbon steel, presumably containing some austenite, and are file hard. In some cases the dimensional changes observed over a period of many years do not exceed one hundred thousandth of an inch per inch. A quantitative answer, however, remains to be determined for austenitic steels as suggested by Mr. Brace.

We are particularly fortunate in having comments from a pioneer in research on hardening phenomena, Mr. Portevin. In the thirteen years elapsed since the publication of the classic paper by Portevin and Garvin on the hardening of carbon steels, we have made frequent reference to it. That paper opened a new field for research activity, but progress therein has been much retarded by inherent experimental difficulties. Perhaps a new method of attack such as that recently employed by Davenport and Bain or a new viewpoint such as we have proposed will stimulate renewed activity.

Referring to his discussion now, one must agree with Mr. Portevin that autographic recording of dilatometric curves is preferable. It is, however, hardly essential in this case where the major object is to relate transformation temperatures with composition to use autographic recording solely for the purpose of obtaining better accuracy of temperature observation than ± 5 degrees Cent. A range in transformation temperature of 10 degrees Cent. corresponds roughly to 0.02 per cent carbon content and variation of carbon content to that extent must be expected within each alloy.

It gives us great pleasure to accord Mr. Portevin recognition for finding the pearlitic structure in the constituent formed on quenching which is usually called troostite. Evidently we should consult *Comptes Rendus* as systematically as *Revue de Metallurgie*.

The relation of Ar″ to equivalence ratios is certainly valid only for well defined conditions of cooling. We might be more explicit than in the text and say: the start of Ar″ is determined for the minimum cooling rates at which no detectable carbide precipitation occurs or for faster rates of cooling. It is assumed, of course, that the temperature of the transformation does not vary materially over a wide range of cooling rates from the minimum upward. That has not been demonstrated in a conclusive manner, but is supported by our experience with carbon-free alloys. As will be shown presently the high carbon alloys must behave towards rate of cooling in a strictly analogous manner to the carbon-free alloys when cooled at the minimum rate or faster than the minimum just defined.

It is certainly advantageous, as Mr. Portevin suggests, to have the "characteristic curve" of a steel rather than the temperature of Ar″ as evaluated here. We do not concede, however, that this temperature is not a fundamental and reproducible characteristic property of a steel just as are the critical points for slow rates of temperature change. This critical temperature, of course, does not have the same wide range of practical utility as do the critical temperatures for slow cooling. We are indebted to Messrs. Bain and Davenport, however, for pointing out a situation where the temperature of Ar″ may be used to practical advantage. They have shown that the properties obtained by retarded cooling through Ar″ are markedly different from those obtained by a normal quench followed by tempering to the same hardness. From the observations of Goss the mechanical properties after the retarded quench are undoubtedly superior. To apply this treatment effectively one must know at what temperature Ar″ will start under the conditions of experiment defined here.

Perhaps much of the divergence in opinion concerning our results may be dissipated by stating more fully our views regarding the sequence of reactions in high carbon steels cooled rapidly enough to suppress Ar_1. Consider a steel containing 0.8 per cent carbon and 3.0 per cent manganese. Cooled from above the solvus temperature, Ar″ will start at 100 degrees Cent. according to Fig. 11. If cooled at a rate faster than necessary to prevent carbide precipitation, the temperature at which Ar″ starts will change no more than if the carbon were replaced by some element having an equivalent effect plus unlimited solid solubility in austenite. Suppose, however, cooling is stopped

for a substantial time at any temperature below the solvus but well above 100 degrees Cent. Then some carbide will separate and reduce the mean solid-solution carbon concentration to say 0.74 per cent. Ar″ will now start on further cooling at 200 degrees Cent. or higher if the carbon distribution is not uniform. The same is true if the solid-solution carbon content is diminished by holding at a temperature between 100 and 200 degrees Cent. except that the transformation will then start while being held as Dr. Eckel has so aptly shown.

Conceding the foregoing statement, one may conclude at once that the reactions with time at holding temperatures above our "start of Ar″," but below the Ar_1 level, are controlled entirely by carbide precipitation. Solid solution carbon dominates the Ar″ transformation. It cannot start until a certain minimum carbon separation occurs. This is the only significant difference between Ar_3 in carbon-free alloys and high carbon steels. It provides an explanation for the characteristic shapes of Davenport and Bain's curves of reaction time versus temperature. The time in which the reaction proceeds to a certain stage increases logarithmically with diminishing temperature below Ar_1 as one would expect were the reaction carbon precipitation alone. As soon as the holding temperature reaches that of Ar″, however, the transformation starts instantly or nearly so as is shown by the abrupt swing of their curves back towards the time origin. From then on carbon separation follows the Ar″ transformation instead of preceding it.

We are indebted to the discussors of this paper for bringing out clearly the need for certain crucial experiments. Undoubtedly the effect of cooling rate on the start of Ar_3 in carbon-free alloys requires further study. It is fundamental to our understanding of the phenomena of hardening. The stability of austenite at room temperature is also worthy of attention. Probably the truth of the matter is intermediate between the extreme views expressed, that is, the stability of high carbon content austenite depends on how far the start of Ar″ is below room temperature. Experiments such as these will certainly add materially to our knowledge of what might be called the dynamics of steel hardening.

ON THE EQUILIBRIUM A_3 AND A_{cm} POINTS IN PURE CARBON STEELS

By Yap, Chu-Phay

Abstract

The results that are reported in this paper are based on the work of Sato, using a differential dilatometer. New values of A_3 and A_{cm} points have been derived. These appear to be more accurate than those derived by Sato himself. The values that have been obtained are, A_3 (ordinary pure iron) 900 degrees Cent.; A_1, 720 degrees Cent.; A_{cm} line, straight line from 0.795 at 720 degrees Cent. to 1.685 per cent carbon at 1130 degrees Cent.

The results obtained by Gutowsky coincide remarkably well with the A_{cm} values derived by the present author.

The A_3 points obtained by Pilling and Halliwell are in good agreement with those of the writer.

Introduction

In connection with certain studies under way, the writer felt a great need for knowing the correct A_3 and A_{cm} lines. A study of the literature reveals the fact that practically no two investigators agree on their results. Epstein[1] recently has called our attention to this state of affairs in his interesting resumé.

It is a common characteristic of all transitions (melting and allotropic transformation) that there is always a hysteresis in the temperature of transition, the lag being proportional to the rate of heating and cooling. Although it will be shown below that when the rate of heating and cooling is very slow, the lag upon heating and cooling at the same rate is equal, no evidence has ever been produced to support this point. While not a true transition, the A_{cm} points will be treated as such throughout this paper. This is justified when we treat austenite as a solid solution and the A_3 and A_{cm} lines as the solubility curves of ferrite and Fe_3C in austenite. On account of the restricted atomic mobilities, it is to be expected that we will find a

[1] S. Epstein, "The Cementite Solubility Line," *Metals and Alloys*, Vol. 1, 1930, p. 559.

The author, Yap, Chu-Phay is a member of the society and is consulting physical metallurgist-chemist, New York City. Manuscript received June 27, 1931.

greater lag in transitions occurring in the solid state. We are therefore quite justified in saying that one of the main causes of the disagreement in the results of thermal, magnetic, resistance and dilatometric analyses, must be due to the different rates of heating and cooling.

The A_3 and A_{cm} Points from Dilatometric Analysis

Realizing that the lag in the critical points is a function of the rate of heating and cooling, Sato attempted to evaluate properly this influence on the A_3 and A_{cm} points in steels. He accordingly carried

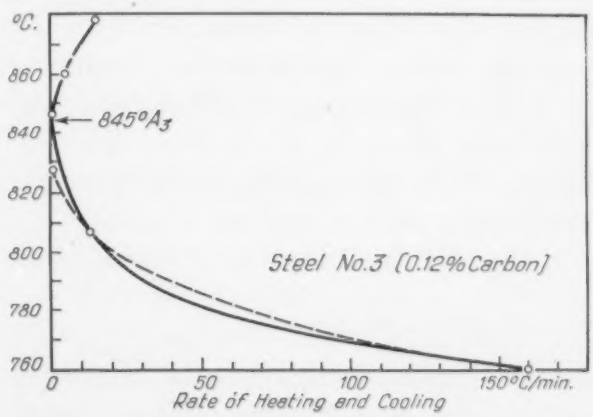


Fig. 1—Observed Critical Points, Ac_3 and Ar_3 Plotted Against the Rate of Heating and Cooling; Whence Sato Obtained 845 degrees Cent. as the Equilibrium Critical Point.

out a series of elaborate and careful experiments,[2] in which he varied the rate of heating and cooling. His data appear to be of a high degree of accuracy and it seems, therefore, more logical to examine critically the so-called equilibrium values he obtained as the result of his investigation. He used practically pure iron-carbon alloys in his experiments and considering the degree of accuracy of his instrument (a differential dilatometer) the effect of the minute amounts of manganese, silicon, phosphorus and sulphur may be safely disregarded. His results may generally be considered as accurate to $\pm$ 1 degree Cent. Even if the instrument is only accurate to $\pm$ 3 degrees Cent. the total degree of error will be much less, as a positive error of 3 degrees Cent. upon heating will be correspondingly counteracted by a negative error of 3 degrees Cent. upon cooling. The only

[2] T. Sato, "On the Critical Points in Pure Carbon Steel," Technical Reports, Tohoku Imperial University, Vol. 8, p. 27, 1929.

criticism of Sato's experimental technique which the present writer is inclined to make is that the dilatometric method is not quite suitable for the accurate determination of the critical points of steels near the eutectoid composition. He arranged his experiments according to the following scheme:—

I. Hypoeutectoid steels:—

- A. Specimen inserted in furnace preheated to 1000 degrees Cent. (1830 degrees Fahr.) and electric current increased immediately in order to raise the temperature.
- B. Specimen heated at the rate of 5 degrees per minute.
- C. Specimen heated at the rate of 0.5 degrees per minute.
- D. Specimen heated to 950 degrees Cent. in furnace, then the furnace is removed and specimen is allowed to cool in the silica tube.
- E. Specimen allowed to cool in furnace after current is turned off.
- F. Specimen cooled at the rate of 0.05 degrees per minute.

II. Hypereutectoid steels:—

- G. Specimen heated at the rate of 20 degrees per minute.
- H. Specimen heated at the rate of 10 degrees per minute.
- I. Specimen heated at the rate of 2 degrees per minute.
- J. Specimen cooled in the furnace.
- K. Specimen cooled at the rate of 10 degrees per minute.
- L. Specimen cooled at the rate of 2 degrees per minute.

On account of the danger of decarburization of hypereutectoid steels upon prolonged heating (the equivalent of annealing), Sato adopted a comparatively more rapid rate of heating and cooling than in the case of hypoeutectoid steels. The results Sato obtained are shown in Tables I and II. He then plotted his thermal data against the rate of cooling as shown in Fig. 1 and then drew curves in such a way that they intersect each other at the Y-axis. The point of intersection as shown in Fig. 1, is then according to Sato the true equilibrium point (temperature of transition). Sato entirely disregarded his "L" values, which are more important than, say, the "J" values obtained at a fairly rapid rate of cooling. According to the physical interpretation of Sato's curves, the true equilibrium point of transition is obtained at zero rate of heating or cooling.

Table I

The Critical, Ac_3 and Ar_3, Obtained Under Varying Conditions of Heating and Cooling

		Critical Points					
			Ac_3			Ar_3	
No.	% C	A†	B	C	D	E	F
1	..	922	911	904	882	891	896
2	0.04	906	890	880	818	850	868
3	0.12	878	860	846	760	807	827
4	0.22	850	828	817	726	780	796
5	0.32	830	805	789	706	758	777
6	0.39	814	791	779	693	745	766
7	0.42	810	780	765	680	736	753
8	0.45	808	776	764	684*	730	748
9	0.62	784	755	746	674*	707	724
10	0.74	774	749	738	674*	704*	719

*Somewhat uncertain; they are obtained from Sato's curves.
†Initial letters refer to heating and cooling rates as set forth on page 262.

The writer thought that some better way of obtaining the equilibrium transition temperature could be found, and in his attempt to find some empirical formulæ which will mathematically express the conditions of the change in the temperature of transition with respect to the rate of cooling, it was found that by simply plotting Sato's data on log-log paper symmetrical figures are obtained. Thus, upon replotting Fig. 1, it now appears as shown in Fig. 2. It is of interest to note that as the rate of heating and cooling is decreased, the temperature of transition thus obtained will approach each other, and that only at an infinitely slow rate of heating and cooling will we obtain the equilibrium transition temperature. A close study of Fig. 2 shows that the figure is not strictly symmetrical, but if we shift the upper curve horizontally to the right very slightly, the figure then becomes strictly symmetrical. This is easily explained on the assumption that the effect of superheating is slightly smaller than those of undercooling as the Ac points are at a higher temperature than the Ar

Table II

The Ac_{em} and Ar_{em} Points Obtained Under Varying Conditions of Heating and Cooling

		Critical Points					
			Ac_{em}			Ar_{em}	
No.	% C	G†	H	I	J	K	L
11	0.92	807	805	790	717*	730	764
12	1.07	875	875	868	820	832	844
13	1.12	902	902	888	840	854	860
14	1.24	945	945	934	890	906	915
15	1.33	998	996	986	920	942	948
16	1.55	1088	1080	1080	1018	1036	1048

*Somewhat uncertain; obtained from Sato's curve.
†Initial letters refer to heating and cooling rates as set forth on page 262.

points; that is, the undercooling represented by the 0.5 degrees Cent. per minute rate is equivalent to about 0.65 degrees Cent. per minute rate upon heating. The correction involved may, however, be safely disregarded as it is very small.

In Table III, the real equilibrium temperatures obtained by Sato are shown in comparison with those derived by the writer according to the method shown in Fig. 2. While the difference in the two sets

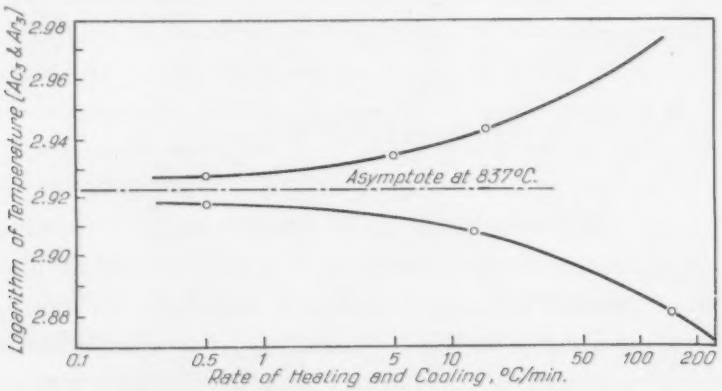


Fig. 2—Critical Points Shown in Fig. 1 Plotted on Log-Log Scale. The Asymtotic Value of 837 degrees Cent. is the True Equilibrium A_3 Point, Instead of 845 degrees Cent. Obtained by Sato.

of values is small in the case of the A_3 points, the A_{cm} values differ as much as 16 degrees Cent., which is considerable when we take into account the fact that the observed thermal data are accurate to $\pm$ 1 degrees Cent. In general the equilibrium values obtained by the writer has the same degree of accuracy as is claimed for the observed data.

It is somewhat unfortunate that no steel between the composition of 0.74 and 0.92 per cent carbon was investigated in order to help us

Table III
The Values of A_3 and A_{cm} Obtained by Sato in Comparison With Those Derived by the Writer

Steel No.	1	2	3	4	5	6
Sato's A_3	903	880	845	815	788	773
Writer's A_3	900*	873*	837*	807*	782*	773*
Steel No.	7	8	9	10	..	..
Sato's A_3	767	764	744	735	..	..
Writer's A_3	759*	755*	753*	728**	..	..
Steel No.	11	12	13	14	15	16
Sato's A_{cm}	786	863	885	941	984	1080
Writer's A_{cm}	780**	856*	870*	925*	968*	1070**

*With an accuracy of $\pm$ 1 degrees Cent.
**With an accuracy of $\pm$ 2 — 3 degrees Cent.

determine more accurately the eutectoid composition under really equilibrium conditions. For some time, the eutectoid composition is accepted as 0.85 to 0.90 per cent carbon by weight, although it should be apparent to anyone that the eutectoid composition changes according to its previous history (i. e. heat treatment). If we can locate the equilibrium A_1 temperature accurately, we should be able to locate with some certainty the equilibrium eutectoid composition as will be shown below.

According to Sato, the eutectoid temperature is located at 726 degrees Cent. (1340 degrees Fahr.), but a study of Fig. 3 shows that

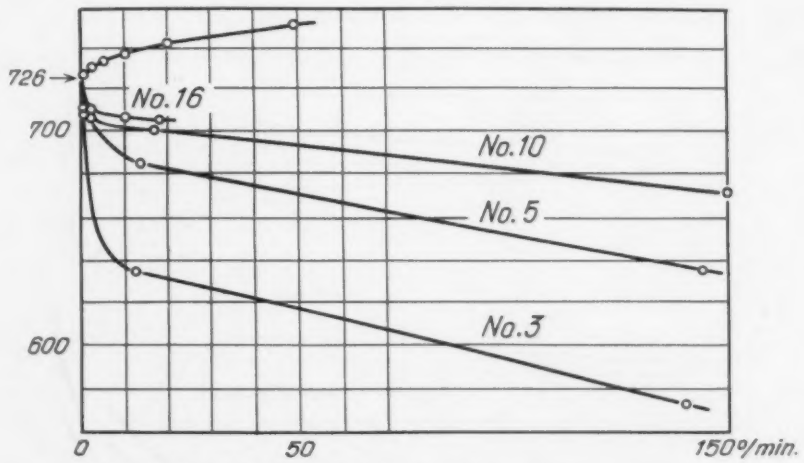


Fig. 3—Sato's Method of Obtaining the Eutectoid Temperature of 726 degrees Cent.

in drawing the Ac_1 and Ar_1 curves, he was evidently influenced by this preconceived idea that the A_1 temperature should be 726 degrees Cent. (1340 degrees Fahr.) as was previously determined by others at the Tôhoku Imperial University. In Fig. 4 (a) and (b) the present writer has shown how we obtain by two separate methods the eutectoid temperature as 720 degrees Cent. (1328 degrees Fahr.). In (a) the points shown in Fig. 3 have been simply replotted. A much more reliable method is shown in (b). Since the eutectoid temperature is more likely to be correct when the bulk (per cent by volume) of the eutectoid is large compared to the bulk of the other constituent, we shall accordingly give more weight to the A_1 of the hypereutectoid steels (Nos. 11-16). The "C" and "F" values of the hypoeutectoid steels are also included because as the rate of heating and cooling of these steels is very slow, they should give fairly close to equilibrium values. In Table IV are shown the mean values of Ac_1

Table IV
The Mean Values of A_1 as Obtained by Sato According to the Rate of Heating and Cooling

	Heating	°C.		Cooling	°C.
C	0.5 degrees per minute	728	F	0.5 degrees per minute	710
H	10.0 degrees per minute	735	K	10.0 degrees per minute	707
1	2.0 degrees per minute	732	L	2.0 degrees per minute	709

and Ar_1 of the different steels, which are plotted in Fig. 4 (b). In this way, we again (and perhaps more convincingly) obtain 720 degrees Cent. (1328 degrees Fahr.) as the eutectoid temperature under similar ideal conditions of infinitely slow rate of heating and cooling. Having determined the eutectoid temperature, the next step would be to determine the eutectoid composition under similar ideal

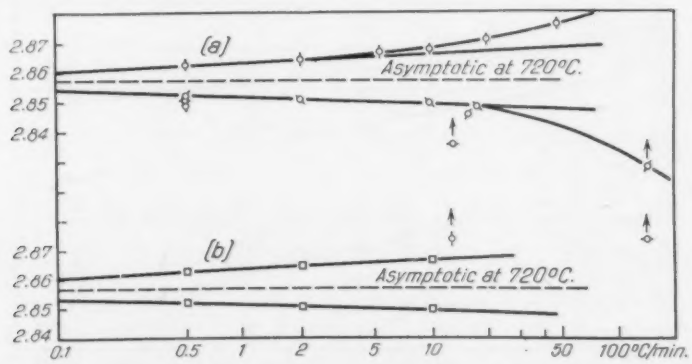


Fig. 4—(a) Fig. 3 Plotted According to Equation 2.
Fig. 4—(b) The Mean Values of Ac_1 and Ar_1 Heated and Cooled at the Rate of 0.5, 2, and 10 degrees per Minute. In both Cases we Obtain 720 degrees Cent. and not 726 degrees Cent. as the Eutectoid Temperature.

conditions. Assuming that between 0.7 and 0.8 per cent carbon there is no abrupt change in the specific heats of alpha iron, Fe_3C and austenite—existing data indicate that this assumption is reasonable—nor in their respective activities, the intersection of the A_3 and A_{cm} curves at 720 degrees Cent. gives 0.795 or simply 0.8 per cent carbon as the eutectoid composition.

The results of some of the more important investigations are also shown in Fig. 5 for comparison. It is interesting to note that the A_{cm} points obtained by Gutowsky[3] as far back as 1909 are in almost perfect agreement with the writer's derived values, while those obtained by Kaya[4] are also in good agreement. We also note that dis-

[3]N. Gutowsky, "Zur Theorie des Schmelz- und Erstarrungsprozesses der Eisen-Kohlenstofflegierungen", *Metallurgie*, Vol. 6, 1909, p. 737.

[4]S. Kaya, "On the Solidus Line in the Iron-Carbon System," *Science Reports*, Tohoku Imperial University, Vol. 14, 1925, p. 529.

regarding the first A_{cm} point near the eutectoid composition (around 1 per cent carbon) we can justifiably consider the loci of Honda's and Endo's[5] and of Konno's[6] critical points to be straight lines parallel to the present writer's A_{cm} curve. Since they were obtained with an appreciably finite rate of heating, it is only reasonable to conclude that they suffered a thermal hysteresis common to all transition. The

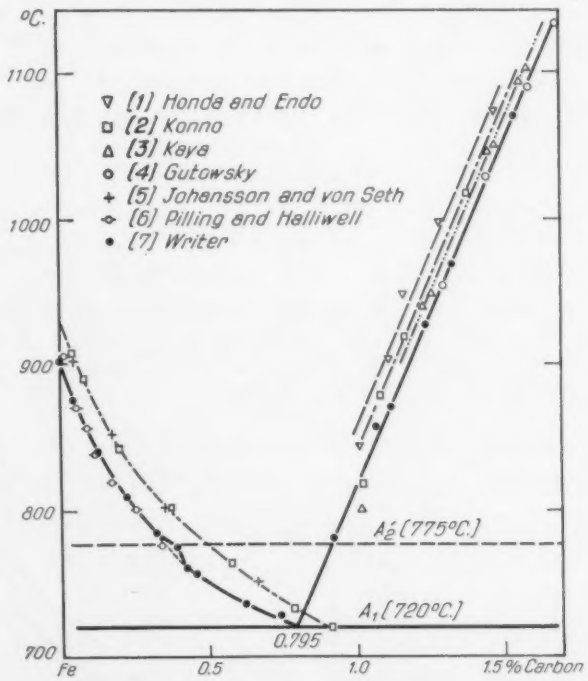


Fig. 5—The A_3, A_1 and A_{cm} Curves as Derived by the Writer from Sato's Data. The Results of Other Investigations are Shown for Comparison. The Agreement between Gutowsky and Pilling and Halliwell Results with Those of the Writer's are Noteworthy.

locus of the A_3 points obtained by Konno runs almost perfectly parallel to the A_3 line obtained by the writer. Points obtained from Johansson's and von Seth's study[7] on the CO–CO_2 equilibria with ferrite–austenite all fall on the locus of Konno's A_3 points. The

[5]K. Honda and H. Endo, "On the Magnetic Susceptibility of the Iron-Carbon Alloys at High Temperatures and the Equilibrium Diagram of the System", *Ibid*, Vol. 16, 1927, p. 627.

[6]S. Konno, "A Study of the A_1 and A_3 Transformation in Carbon Steels by Means of a Differential Dilatometer, *Ibid.*, Vol. 12, 1923, p. 127. According to him, the eutectoid composition is located at about 0.91 per cent carbon, but a careful study of his dilatometric curves reveals that in this particular steel he did not heat it beyond 800 degrees Cent.

[7]A. Johansson and R. von Seth, "The Carburization and Decarburization of Iron and Some Investigations on the Surface Decarburization of Steels", *Journal*, Iron and Steel Institute, Vol. 114, 1926, p. 295.

critical points obtained by Pilling and Halliwell[8] are in almost perfect agreement with the writer's values.

Unfortunately we have not yet definitely established the upper limit of the solid solubility of Fe_3C in austenite at the eutectic temperature. We have generally accepted the result of Gutowsky in placing the limit at 1.7 per cent carbon at 1130 degrees Cent. (2066 degrees Fahr.), although in recent years Honda and his associates have claimed the maximum solubility to be only 1.6 per cent carbon. Assuming 1130 degrees Cent. as the correct eutectic temperature, the maximum solubility is nearer 1.7 than 1.6 per cent, being exactly 1.685 per cent carbon.

Summary

1. Based on the work of Sato, using a differential dilatometer, new values of A_3 and A_{cm} points have been derived, which appear to be more accurate than those derived by Sato himself. The difference is sometimes as high as 16 degrees Cent.

2. The following important values have been obtained:

(a) A_3 (ordinary pure iron), 900 degrees Cent. (1652 degrees Fahr.).

(b) A_1, 720 degrees Cent. (1328 degrees Fahr.) and 0.8 per cent carbon.

(c) A_{cm} line, straight line from 0.795 at 720 degrees Cent. (1328 degrees Fahr.) to 1.685 per cent carbon at 1130 degrees Cent. (2066 degrees Fahr.).

3. The results of previous investigations have been shown for comparison and discussed. It is noted that the results obtained by Gutowsky coincide remarkably well with the A_{cm} values derived by the writer, while the A_3 points obtained by Pilling and Halliwell are likewise in very good agreement.

4. It may be claimed with some confidence that the values of A_3 and A_{cm} points derived by the writer represent probably the most accurate ones so far obtained.

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[8] I am greatly indebted to Mr. Marsh for furnishing me with the points obtained by Pilling and Halliwell, Westinghouse Electric & Mfg. Co., *Technical Reports*, L-2,612 (1924). It is my understanding that they used quite pure iron-carbon alloys.

THE TEMPERATURE ATMOSPHERE PROBLEM IN HIGH SPEED STEEL

By Sam Tour

Abstract

A study is made of the effect of variations in oxygen and carbon monoxide content in the high heat furnace upon the structure of high speed steel treated at 2400 degrees Fahr. (1315 degrees Cent.) in this furnace. Indications are that the structure resulting from the high heat treatment is materially affected by the oxygen and carbon monoxide content of the furnace atmosphere during heat treatment and that the furnace atmosphere shifts the equilibrium diagram for standard 18-4-1 high speed steel. It is further indicated that unless very careful atmospheric control is obtainable that 2400 degrees Fahr. is probably too high a temperature to use in the heat treatment of standard 18-4-1 high speed steel and that possibly 2360 degrees Fahr. (1295 degrees Cent.) is the better for general practice.

Introduction

THE literature in connection with the heat treatment of high speed steel is considerable. No attempt will, therefore, be made to review the entire literature on the subject, but specific attention is directed to certain very excellent publications which are enumerated in the appendix to this paper.

In a paper entitled "The Heat Treatment of Delicate Tools of High Speed Steel"[1] by the author, it was pointed out that furnace atmospheres have something to do with grain growth in high speed steel during heat treatment and that with proper control of furnace atmospheres not only can the surface condition of the steel be protected, but undue grain growth can be eliminated without the sacrifice of satisfactory red hardness in the finished tool.

[1]Sam Tour, "The Heat Treatment of Delicate Tools of High Speed Steel," *Fuels and Furnaces*, September, 1930.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3-7, 1932. The author, Sam Tour, is a member of the society and vice-president of Lucius Pitkin, Inc., 47 Fulton St., New York City. Manuscript received July 29, 1932.

Pseudo-Binary Diagram of High Speed Steel

The pseudo-binary diagram for high speed steel as developed by Grossmann and Bain in "High Speed Steel" is shown in Fig. 1. This is a very valuable diagram for consideration. Standard high speed steels of the 18-4-1 type can be considered as falling in the neighborhood of 30 to 35 per cent of complex carbides as indicated

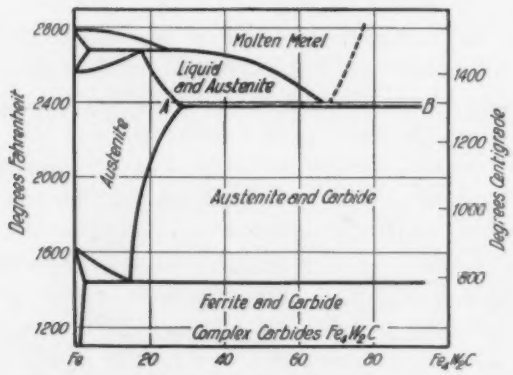


Fig. 1—The Pseudo-Binary Diagram of Fe-Fe_4W_2C.

on this chart. The important item of consideration is the location with regard to temperature of the line A-B and the significance of this line. Grossmann and Bain show it at a temperature of 1300 degrees Cent. (2372 degrees Fahr.). If high speed steel containing the equivalent of 28 or more per cent of the complex carbide is heated above this line A-B, liquid eutectic will be formed. In other words, if in actual practice high speed steel tools were actually heated to 2400 degrees Fahr. incipient melting should result. If the maximum heat treating temperatures are kept below the line A-B then no liquefaction is to be expected and the structure should be austenite and carbide with the austenite carrying the maximum amount of carbide in solution that is possible. In other words, high speed steel heated to temperatures just below the line A-B will have maximum carbides in a solution of austenite saturated with carbide for that temperature.

In the work reported in this paper, no attempt has been made to check the exact location of the line A-B, but an effort has been made to determine whether or not the line A-B is shifted with respect to temperature by a change in the furnace atmosphere. If at one furnace atmosphere, we find liquefaction for a given temperature and in another furnace atmosphere, but at the same temperature for the

same period of time, no liquefaction occurs then it seems that the line A-B has indeed been shifted by the change in furnace atmosphere.

The Method

All of the pieces used in this work were taken from one bar of annealed standard 18-4-1 tungsten high speed steel. A 1-inch bar of hot-rolled and annealed steel was turned down to approximately ¾ inch diameter in order to remove all surface skin. Pieces approximately 1 inch long were cut off and a V-shaped notch approximately $\frac{1}{16}$ inch thick was turned in at the center of each of these

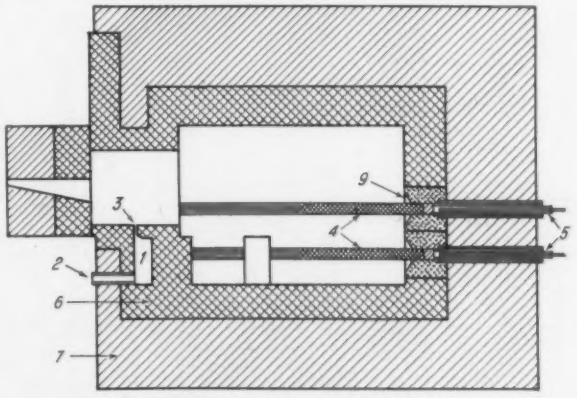


Fig. 2—Diagram of Certain Curtain Control.

1. Atmosphere Combustion Chamber
2. Inlet from Manometer
3. Slot Emitting Curtain of Combusted Gases
4. Globar Heating Elements
5. Water Cooled Terminals
6. Refractory Lining
7. Heating Insulation
8. Hearth Plate (Not Shown)
9. Terminal Bricks.

1-inch pieces. Serial numbers were stamped on each end of each piece together with the letter A at one end and the letter B at the other end so as to be able to identify the pieces throughout the work.

All pre-heating was done in a metallic resistor electric furnace of the certain curtain type built by C. I. Hayes, Inc., and equipped with manometer tubes to indicate and control the proportion of gas and air used to maintain the furnace atmosphere.

All of the high heat treatments were carried out in a Globar heated electric furnace of the certain curtain type as built by C. I. Hayes, Inc., and equipped also with manometer tubes for indication and control of the gas-air ratios used for maintaining the furnace atmosphere. A diagram of this furnace and the method of atmosphere control is shown in Fig. 2. In Fig. 3 is shown the

manometer tubes as used for control of the gas and air being admitted to the combustion chamber underneath the door of the furnace. In Fig. 4 is shown a diagram of the carbon monoxide–carbon dioxide–oxygen relationship in this furnace when operating at a temperature of 2400 degrees Fahr. (1315 degrees Cent.) with various

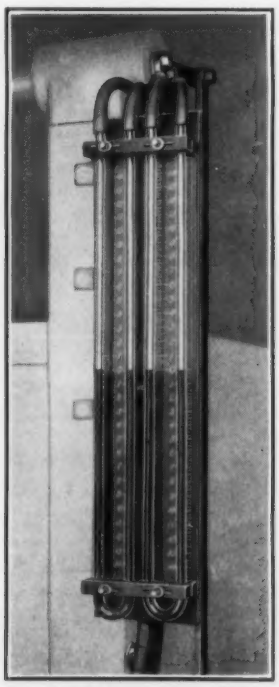


Fig. 3—Manometer Tubes, Controlling Gas and Air Entering Combustion Chamber.

proportions of air being admitted for a given proportion of gas. The chart of furnace atmospheres for given settings as indicated in Fig. 4 was not accepted in whole for the work reported upon in this paper, but actual orsat analyses were made for each individual heat treatment.

All samples were pre-heated for 30 minutes at 1600 degrees Fahr. (870 degrees Cent.) in an atmosphere which showed on analyses to contain 3 per cent of oxygen and 11.8 per cent of carbon dioxide and no carbon monoxide. Pieces for the hardening treatment were treated for periods of time as indicated, at temperatures as indicated, and in atmospheres as indicated. For each condition of atmosphere at the higher temperature, the valves were adjusted and the furnace allowed to operate for several minutes and then orsat

analyses made of the atmosphere, then, after this was found satisfactory, the piece to be hardened, or pieces, were inserted and the hardening accomplished after which orsat readings again were taken to make sure that the atmospheric conditions had not changed during the period that the specimens under test were in the high heat. Samples for gas analyses were withdrawn through a nickel tube,

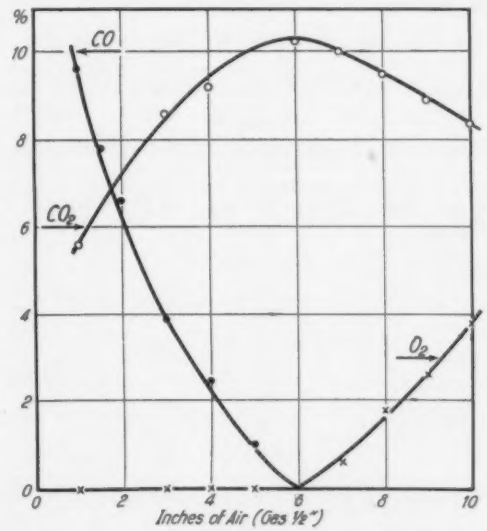


Fig. 4—Atmosphere Relationship in Certain Curtain Type Furnace, When Operating at 2400 Degrees Fahr. (1315 Degrees Cent.).

a considerable quantity being flushed through the apparatus each time to make sure that a true sample from the heating chamber itself was being analyzed. The inlet end of the nickel tube in each case was at the center of the furnace where the samples being heat treated were to be placed. Previous work had indicated that practically no variation in furnace atmosphere exists in the region where work is being heated in these furnaces.

After heating for the indicated time, the specimens were withdrawn from the furnace with a pair of tongs and quenched in quenching oil till cold, then washed and dried. After noting the surface appearance of the samples, they were fractured along the V notch which had been cut in previously and the A portions set aside and the B portions were all drawn at 1050 degrees Fahr. (565 degrees Cent.) for one hour in a Homo electric furnace. All A and B portions were then examined metallographically after etching with 5 per cent nital solution to develop the grain boundaries. A uniform

etching time was not practiced but in each case etching was continued to develop properly the grain boundary structure.

Results

No attempt is made in this paper to tabulate all of the samples which were run, nor to show photomicrographs of all the structures obtained. The significant ones are tabulated in Table I, together with remarks as to the appearance of the fracture of the specimens

Table I

18-4-1 High Speed Steel—Preheated 30 min. 1600 Degrees Fahr.—3 Per Cent O_2

A—As quenched specimen.
B—As quenched and drawn 1 hour at 1050 degrees Fahr.

Fig. No.	Specimen No.	Hardening Temperature Degrees Fahr.	Time in furnace	CO_2	O_2	CO	Remarks
5	6-A	2300	10	8.2	0	5.1	Fine Grain. Surface O.K.
6	4-A	2300	10	10.8	.8	0	Fine Grain but some surface scale.
7	1-A	2300	10	0	18	0	Grain growth. Scaled.
8	19-A	2360	3	6.2	0	6.5	Fine grain. Surface O.K.
9 10	15-A 15-B	2400	3	8.1	0	10.3	Very slight grain growth. Surface O.K.
11 12	14-A 14-B	2400	10	8.1	0	10.3	Some grain growth. Surface slight scale.
13 14	13-A 13-B	2400	10	9.6	0	4.6	Great grain growth. Eutectic forming in spots. Surface scaled.
15 16	12-A 12-B	2400	10	8.8	0	2.8	Great grain growth. Numerous eutectic areas and larger. Scaly.
17 18	11-A 11-B	2400	10	11.4	0	0	Considerable eutectic formation; badly scaled.
19 20	10-A 10-B	2400	10	8	4.2	0	50% transformed; very badly scaled.
21 22	8-A 8-B	2400	10	0	18.4	0	100% transformed. Almost scaled away.

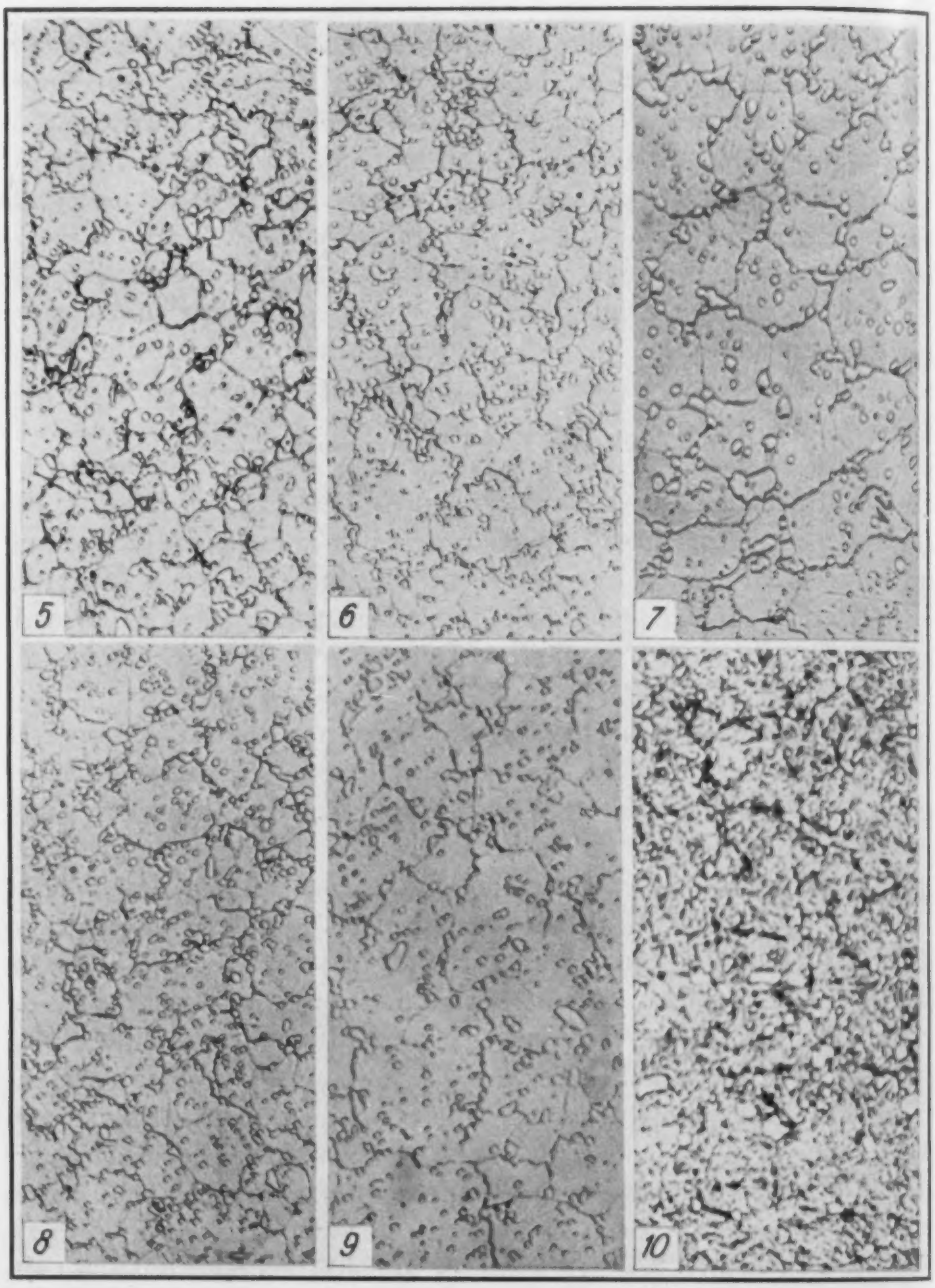
as hardened, the surface appearance of the specimens as hardened and a brief note regarding the amount of eutectic found on metallographic examination. Photomicrographs at 500 diameters magnification are shown of each of the specimens indicated in Table I.

Discussion

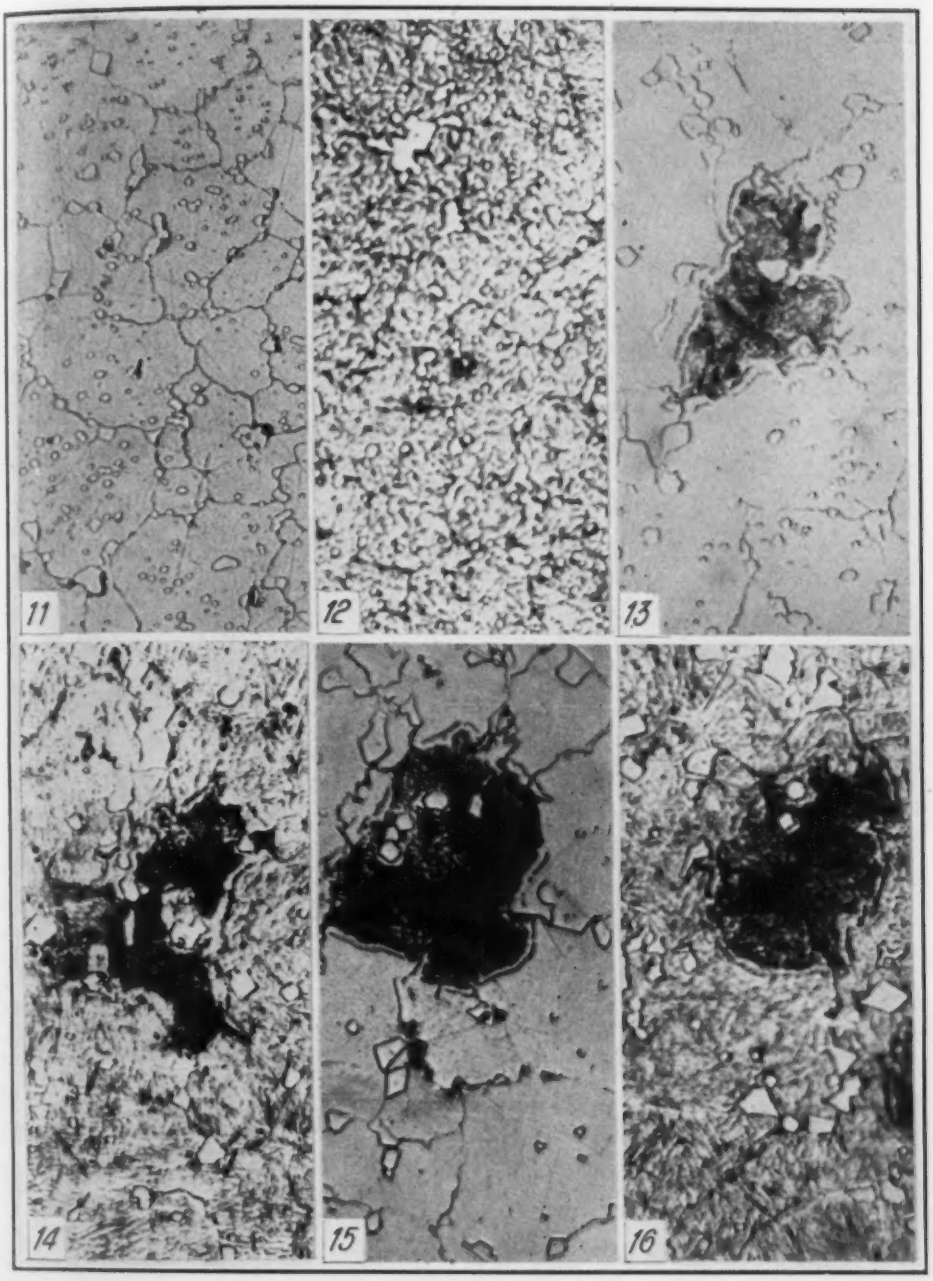
Specimen 6 as heated to 2300 degrees Fahr. (1260 degrees Cent.)

for ten minutes in an atmosphere containing approximately 5 per cent carbon monoxide came out with fine clean surface, a fine grain fracture and a structure as indicated in Fig. 5. Specimen 4 treated to the same temperature and for the same time as specimen 6 but in an atmosphere containing no carbon monoxide and 0.8 per cent of oxygen showed a similar fine grain fracture but some surface scale from the heat treatment and a structure as indicated in Fig. 6 showing a somewhat, although not decidedly, larger grain size than resulted from the treatment given to specimen 6. Specimen 1 treated for the same time and at the same temperature as specimens 4 and 6, but in an atmosphere of air containing 18 per cent oxygen showed decided grain growth as indicated by a coarse fracture, decided scaling of the surface and also a decided grain growth as indicated by Fig. 7. Specimen 19 was heat treated to 2360 degrees Fahr. (1295 degrees Cent.) for three minutes only in an atmosphere containing 6.5 per cent of carbon monoxide resulting in a fine grain structure, a satisfactory surface and a grain size as indicated in Fig. 8. Practically no grain growth is indicated for this treatment in this atmosphere.

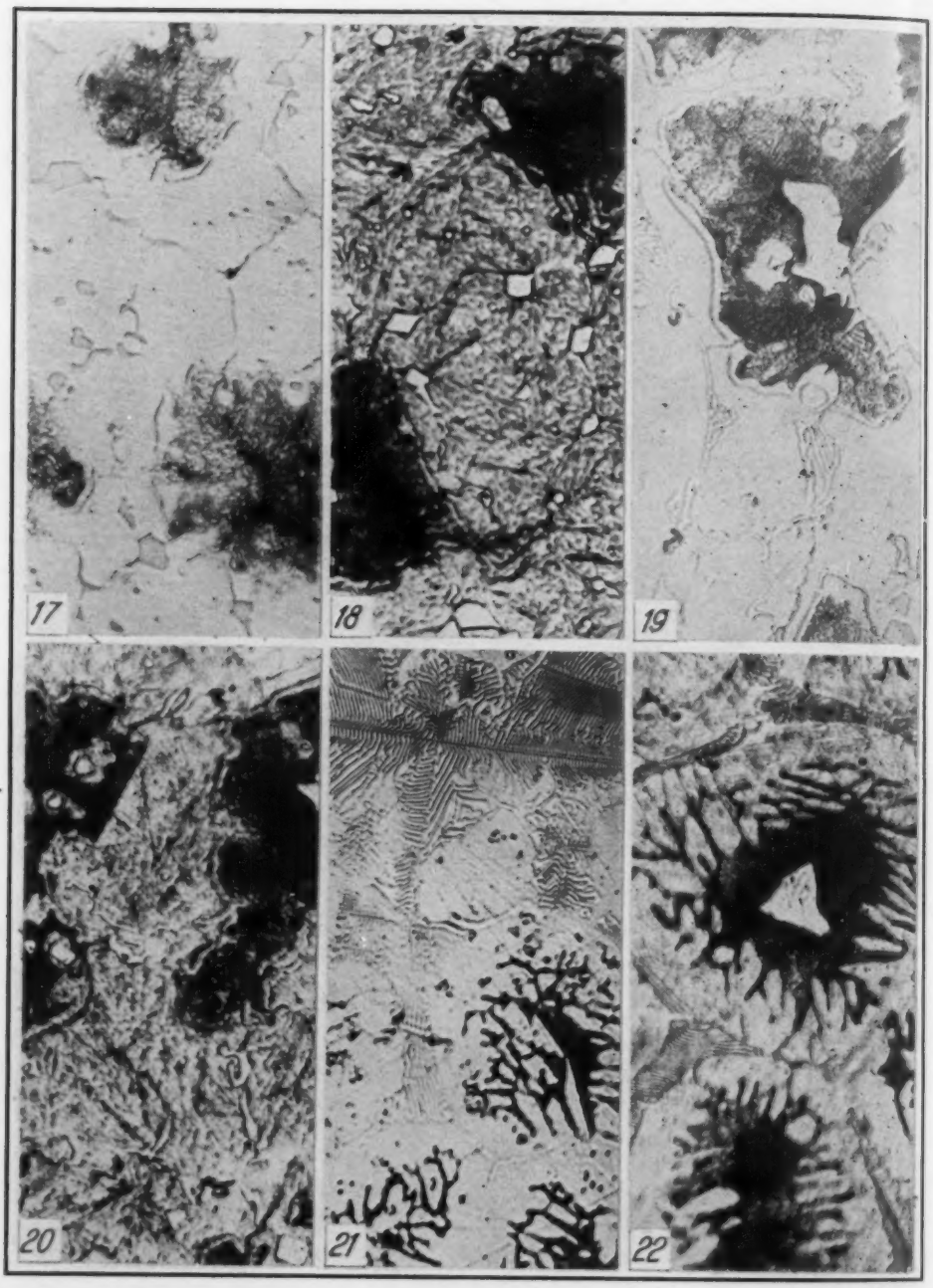
Specimen 15 was heated for only three minutes to 2400 degrees Fahr. (1315 degrees Cent.) in an atmosphere containing 10.3 per cent of carbon monoxide and showed on fracture only very slight coarsening of the grain, a satisfactory surface after heat treatment, and a grain growth and a certain amount of coalescence of carbides as indicated by Fig. 9. The structure of this specimen after drawing at 1050 degrees Fahr. (565 degrees Cent.) for one hour is shown in Fig. 10. Specimen 14 was heated for ten minutes at 2400 degrees Fahr. (1315 degrees Cent.) in an atmosphere containing 10.3 per cent of carbon monoxide, the fracture showing some coarsening of the grain, and the surface a very slight amount of scale, and the structure as indicated in Fig. 11 shows a considerable grain growth but no apparent intercrystalline liquefaction. Fig. 12 shows the structure of specimen 14 after the drawing treatment. Specimen 13 was heated for ten minutes at 2400 degrees Fahr. (1315 degrees Cent.) in an atmosphere containing 4.6 per cent of carbon monoxide instead of the 10.3 per cent used on specimen 14. The surface of the specimen showed considerable scale, the structure as indicated in Fig. 13 shows very great grain growth and the formation of some eutectic indicating the starting of intercrystalline liquefaction. The structure of this specimen after drawing and near



one of the eutectic areas is shown in Fig. 14. Specimen 12 was also heated for ten minutes at 2400 degrees Fahr. (1315 degrees Cent.) but in an atmosphere containing 2.8 per cent of carbon monoxide instead of the higher percentages used in the previous two specimens described. Enormous grain growth resulted and numerous



eutectic areas of larger proportions than found when an atmosphere containing roughly 5 per cent of carbon monoxide was used. The structure of the specimen as hardened is shown in Fig. 15 and as drawn in Fig. 16. The eutectic areas are larger and more numerous. Specimen 11 was also treated for ten minutes at 2400 degrees



Fahr. (1315 degrees Cent.) but in an atmosphere containing no carbon monoxide and no oxygen and 11.4 per cent of carbon dioxide. This specimen was badly scaled and a very considerable amount of eutectic structure was formed as indicated by Fig. 17 of the as quenched portion and Fig. 18 of the as drawn portion. Specimen

10 was also treated for ten minutes at 2400 degrees Fahr. (1315 degrees Cent.) but in an atmosphere containing 4.2 per cent of oxygen and 8 per cent of carbon dioxide. This specimen was very badly scaled indeed and the structure showed fully 50 per cent of the material had been changed over to the eutectic formation. The structure as quenched is shown in Fig. 19 and as drawn in Fig. 20. Specimen 8 was similarly treated for ten minutes at 2400 degrees Fahr. (1315 degrees Cent.) but in air containing 18.4 per cent of oxygen and no carbon monoxide. The specimen almost scaled away in this treatment and the resulting structure shows practically 100 per cent formation of the eutectic. The as quenched structure is shown in Fig. 21 and the as drawn in Fig. 22.

The more active formation of the eutectic as indicated by specimens 8 and 10 treated in atmospheres containing considerable oxygen or even in specimen 11 treated in an atmosphere containing considerable carbon dioxide and no carbon monoxide, might be attributed to self-heating as the result of the burning of iron to iron oxide on the surface of the specimens. Sufficient self-heating, however, to result in any appreciable increase in the actual temperature of a specimen of this size could hardly be expected, however, in an atmosphere containing 2.8 per cent of carbon monoxide as in specimen 12 or 4.6 per cent as in specimen 13.

Conclusion

It would seem as though the above work indicates that the line A-B referred to previously in connection with Fig. 1 is actually shifted by the change in the furnace atmospheres and that for low carbon monoxide content this line is below 2400 degrees Fahr. (1315 degrees Cent.) and, for a carbon monoxide content of around 10 per cent, this line is slightly above 2400 degrees Fahr. (1315 degrees Cent.). If we assume that the line is normally at about 1300 degrees Cent. (2372 degrees Fahr.), as indicated by Grossmann and Bain, then we should make sure that all high speed steel is treated either below this temperature or else in an atmosphere containing sufficient carbon monoxide to raise this critical temperature sufficiently so that for the temperature actually used no eutectic formation results.

That the approach to this line A-B is also effected by furnace atmospheres is indicated in the amount of grain growth resulting at temperatures of 2300 degrees Fahr. (1260 degrees Cent.). The

rate of grain growth might be considered as a function of how near the specimen is heated to the line A-B. If the line A-B is shifted upward by an atmosphere containing considerable carbon monoxide, then we can safely heat steel to a higher temperature for heat treatment without serious grain growth.

ACKNOWLEDGMENTS

The writer gratefully acknowledges the co-operation of A. H. Kingsbury of the Crucible Steel Co. in supplying steel for many of the tests preliminary to the set reported on in this paper, of J. P. Gill of the Vanadium-Alloys Steel Company in supplying the high speed steel used in this investigation, of C. I. Hayes, Inc., in carrying out the heat treatments and gas analyses referred to and in supplying and permitting the use of Figs. 2, 3 and 4, and the services of Herbert Bartow of Lucius Pitkin, Inc., in the metallographic examination. The author also thanks Messrs. Grossmann and Bain for permission to use the diagram shown in Fig. 1.

Appendix

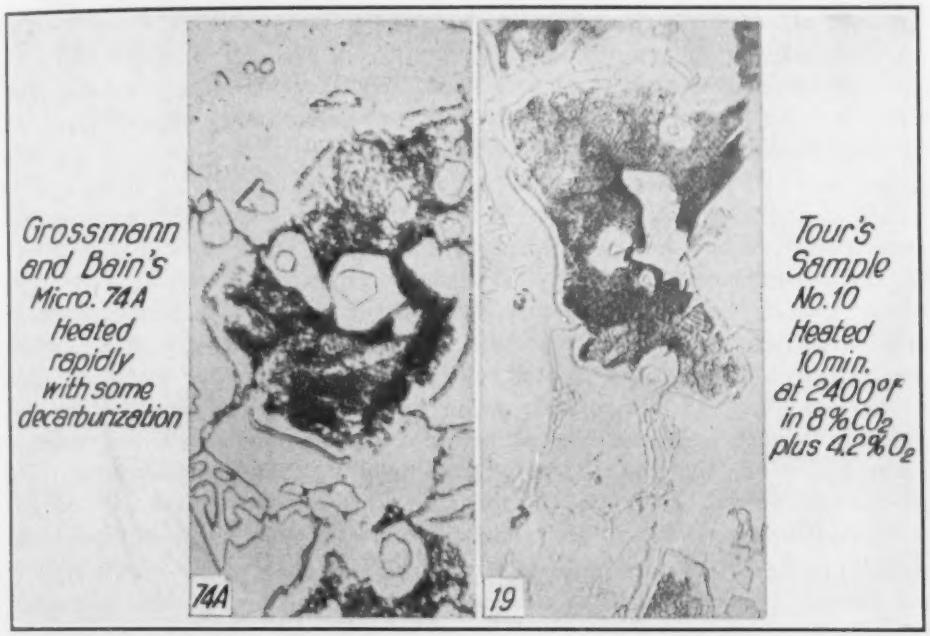
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2. Howard Scott, "Relation of the High Temperature Treatment of High Speed Steel to Secondary Hardness and Red Hardness," Bureau of Standards Scientific Paper No. 395, 1920.
3. B. H. DeLong and F. R. Palmer, "What Happens When High Speed Steel Is Quenched," TRANSACTIONS, American Society for Steel Treating, Vol. XIII, No. 3, March, 1928.
4. M. A. Grossmann, "Dimensional Changes of High Speed Steel in Heat Treatment," TRANSACTIONS, American Society for Steel Treating, 1922, p. 695.
5. G. R. Brophy, R. H. Harrington and A. W. Merrick, "Occurrence of Fish Scale in High Speed Steel," TRANSACTIONS, American Society for Steel Treating, Vol. XVIII, 1930, p. 440.
6. G. R. Brophy and R. H. Harrington, "Nature of Abnormal Grain Growth in High Speed Steel," TRANSACTIONS, American Society for Steel Treating, Vol. XIX, March, 1932.
7. E. C. Bain and W. S. N. Waring, "Austenite Decomposition and Length Changes in Steel," TRANSACTIONS, American Society for Steel Treating, Vol. XV, 1929, p. 69.
8. J. V. Emmons, "Some Physical Properties of High Speed Steel," TRANSACTIONS, American Society for Steel Treating, Vol. XIX, February, 1932.
9. Recommended Practice for the Heat-treatment of 18% Tungsten High Speed Steel," *National Metals Handbook,* 1930 Edition, p. 100.

DISCUSSION

Written Discussion: By E. E. Thum, editor *Metal Progress,* Cleveland. Mr. Tour is to be congratulated for drawing attention to this curious fact,

which has been noted by a number of tool makers, that high speed steel heated in an atmosphere having an excess of carbon monoxide resists burning, overheating, and grain coarsening, and makes a better all-around tool than one heated an equal time and just as hot in an oxidizing atmosphere. One can readily see the reason for a different chemical action at the very surface, but the effect is generally thought to be deep seated, and now Mr. Tour brings definite microscopic evidence that this impression is correct.

His experimental procedure appears well designed to stabilize all the variables except the gas atmosphere. If the changes in microstructure illus-



trated are due to gas, diffusing into the steel, they should be more pronounced near the surface than in deep seated regions. Mr. Tour might clarify this point. Of course, the temperature in these experiments was so high that the speed of gas diffusion is vastly greater than in our well-known case carburizing operations, and the ¾-in. bars may have been penetrated to the very center, but one would be more confident in accepting gas as the sole cause of the grain coarsening, if he had definite assurance that in fairly large sections quenched from an oxidizing atmosphere, the grain is coarsened more near the surface than at the center.

Mr. Tour's plausible hypothesis that oxygen, dissolved in the high speed steel from the hot surrounding atmosphere, lowers the eutectic horizontal (or, in other words, causes an entirely new and more complex eutectic to form which melts at a lower temperature) requires us to accept his statement that the blackened areas in Figs. 13 to 20 represent eutectic which has formed during the heating—that is, spots which have actually melted. In questioning this interpretation of the microstructure, I would refer anyone interested to Messrs. Grossmann and Bain's book "High Speed Steel," in which Figs. 74A and B show

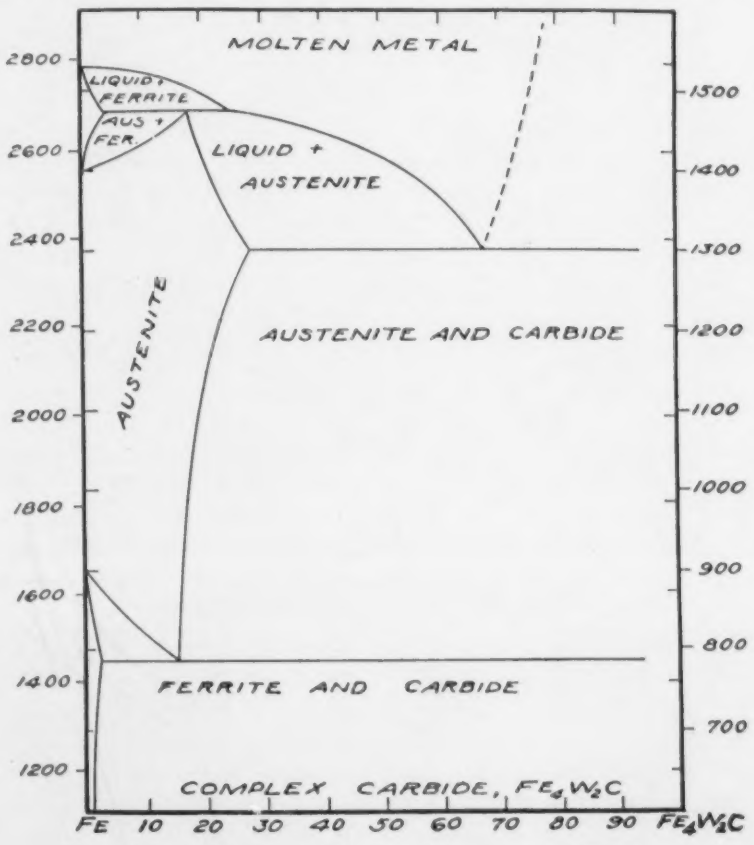
identical structures. These gentlemen say on page 125 "Occasionally, when some decarburization accompanies rapid heating, the carbide diffusion does not suffice to enrich the austenite in carbide elements according to equilibrium conditions, and as a result, some ferrite (delta iron solid-solution) is precipitated within the austenite grains. . . . The behavior serves to call attention to the fact that carbon must be present everywhere in a concentration greater than about 0.45 per cent in order that the solid solution phase may be wholly austenitic at very high temperatures. Photomicrographs 74A and B show such ferrite within the austenitic grains. It is always dark-etching and resembles somewhat very finely divided carbide particles (as sorbite) in the ferrite of carbon steel. It is found whether incipient fusion had occurred or not."

This interpretation of the microstructure can, I think, be correlated with two well-known actions of oxygen in steel. Everyone will admit that the dendrites in high speed steel ingots are badly cored and this nonuniformity of structure runs clear through to the annealed bar. Since the complex carbides diffuse very very slowly at ordinary heating and rolling temperatures it is certain that the austenite in Mr. Tour's samples was quite heterogeneous—places rich in carbide-forming elements exist in fairly close proximity to places low in carbide-forming elements. Oxygen—or mixtures of carbon oxides containing loosely bound oxygen—diffusing into the steel at the temperatures in question would either tend to decarburize the steel somewhat by forming carbon monoxide with carbon from the austenite and oxygen from the atmosphere, or the oxygen would go into solution if the austenite were not already saturated with this element, and there is much evidence to show that oxygen dissolved in ferrite (alpha or delta iron) increases the solubility of carbon. Either of these effects, and especially the two of them working simultaneously, would promote the formation of patches of delta iron solid solution in the austenite (which are these dark etching areas shown by Mr. Tour) where ever it initially was deficient in carbide-forming elements. A glance at the equilibrium diagram indicates that these areas are much more infusible than the eutectic; in fact, delta solid solution would remain solid nearly to 1500 degrees Cent. (2700 degrees Fahr.). Consequently they cannot have melted, as assumed by Mr. Tour. The spots which melt first are the eutectic; its structure is the lamellar area at the top of his micrograph Fig. 21. In that same view I would interpret the clear areas as austenite and the dark gray "worm paths" as delta iron.

If this interpretation of the microstructure is correct it now remains to give a reasonable explanation of why the austenitic grains grow in very hot oxidizing atmospheres and are stable in equally hot carbonaceous atmospheres.

Turning to Jeffries and Archer's "Science of Metals," we find that the principal reason for grain growth is a gradient (nonuniformity) of some sort. For instance, gradients of internal stress or cold work cause coarsening at certain areas and Stead's brittleness results. This cannot be the cause here, for the mixed samples were all cut from the same bar. Disparity of grain size, both relative and absolute, is another potent cause of grain growth, but we must assume that the internal structure of all samples was equivalent, each to each. Differences in temperature or atomic mobility cause grain growth, but all Mr. Tour's samples were heated to 2400 degrees Fahr. for the same time.

Grain growth may be prevented by mechanical obstruction of matter in solution, of insoluble inclusions, or of other constituents. To be effective the obstruction should be finely and uniformly divided. In this high speed steel the effective obstructing substances, if any, are carbon and the carbide-forming elements, and a carbonaceous atmosphere would tend to carbonize low carbon areas, thus more effectively obstructing grain growth, or at least to promote

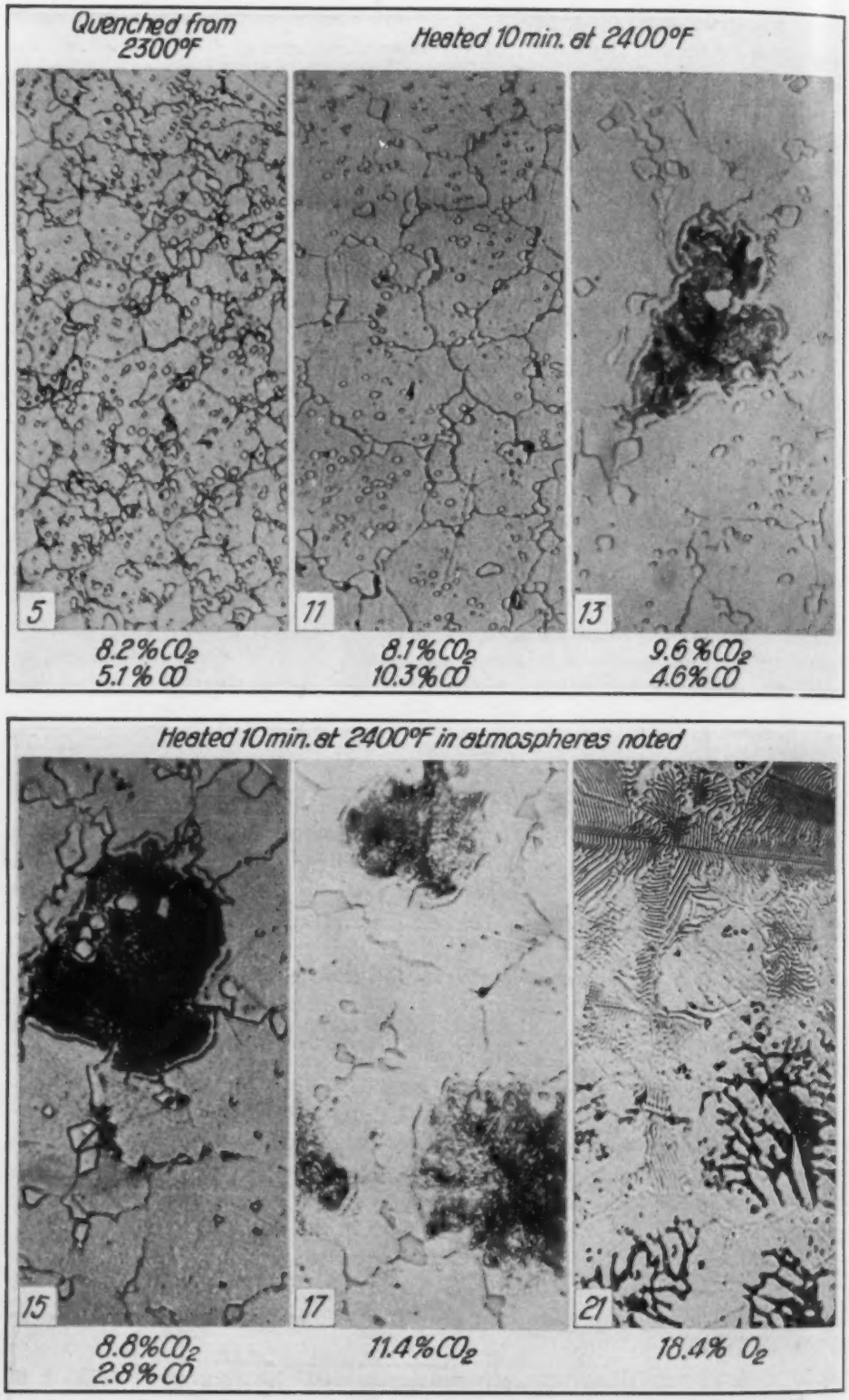


Pseudo-binary Constitution Diagram Fe-Fe_4W_2C.

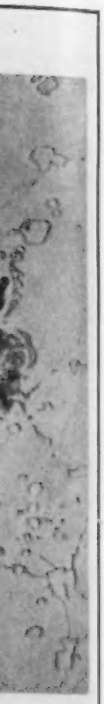
uniformity in the austenite, and hence reduce composition gradients which are undoubtedly great causes for grain growth.

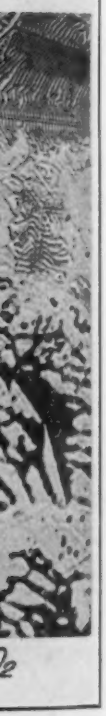
Thus an atmosphere having an excess of carbon monoxide would tend to restrict grain growth by suppressing local differences in concentration. Conversely, an atmosphere having an excess of oxygen will give powerful impetus to grain growth, since, as shown above, it creates numberless patches of delta solid solution in the austenite and this produces steep composition or concentration gradients which favor rapid grain growth in the austenite.

The above theoretical considerations harmonize, I think, with all the observed facts stated by Mr. Tour (except one) and give a logical relation between furnace atmosphere and grain growth in the surface layers, not too deep for gas penetration by diffusion. The one thing yet to explain is the incipient melting shown by small eutectic areas in Fig. 19 and the large scale melting in



Mr. Tour's Photomicrographs Reassembled for Comparison.





Figs. 21 and 22. Sample 8 from which the latter two were taken, according to Table I, was "almost scaled away." This means that the field of Figs. 21 and 22 must have been fairly close to the surface. It is well known that the various elements burn away at various rates, and the very surface of a scaled high speed steel is different in chemical composition from the original bar, and that this also produces composition gradients inward from the surface. There would be no assurance, therefore, that the melted sample shown in photomicrographs Figs. 21 and 22 has the same composition as the others which did not melt—in fact, we may be justified in assuming that it is *not* the same alloy, and in hoping that the spot photographed in Fig. 19 was close enough to the surface of bar 10 to be included in the same explanation. If these assumptions prove incorrect one could still fall back on the idea that such excessive and rapid scaling as occurred on these samples generated enough heat by combustion of the metallic elements to raise the temperature of the remaining core substantially above the indicated furnace temperature (2400 degrees Fahr.), and hence above the eutectic horizontal.

Oral Discussion

H. G. KESHIAN[1]: I have been interested in this paper for its practical value.

Mr. Tour finds no grain growth in the presence of large amounts of carbon monoxide in the furnace atmosphere, and large grain growth in the absence of sufficient amount of that gas in the furnace.

It seems to me that at the absence of certain amount of carbon monoxide in the furnace the actual temperature of the piece itself is higher than the furnace temperature indicated by the furnace pyrometer, and in the other case, where a large amount of carbon monoxide is maintained in the furnace, the actual temperature of the piece itself may even be less than the furnace temperature.

I would like to ask Mr. Tour, therefore, in making his tests whether or not he has taken the actual temperature of the test pieces, by, say, inserting a thermocouple into the test pieces.

C. B. SADTLER[2]: I would like to offer my congratulations to Mr. Tour for his very excellent piece of work. Those of us who spend most of our time working with high speed steels appreciate the character of the work and the fortitude he has shown in pushing into a pioneer field. Mr. Tour brings chemistry into the tool room in a somewhat different way from what it has been brought in before. I mention that because I think that ultimately the whole solution will be made along physico-chemical lines.

I would like to point out that not only are we concerned with the 18-4 and 1 per cents of tungsten, chromium and vanadium respectively but also iron and the minor elements in the steel; and what is more important, I think, in the atmosphere, not only the carbon monoxide and carbon dioxide upon which both Mr. Tour and Mr. Thum have dwelt at some length, but I think it is quite im-

[1]Metallurgist, Chase Companies, Inc., Waterbury, Conn.

[2]Metallurgist, Barber-Colman Co., Moline, Ill.

portant to carry along in your thoughts the fact that hydrogen water vapor and nitrogen are also present in many cases.

I am assuming, of course, that the furnace atmospheres are made from city gas and air. The very fact that in many cases city gas is used presents variations due to the needs of the gas manufacturer. At certain times there may be only a small percentage of water gas, and at other times a larger percentage.

I was impressed by the need for taking these things into consideration in viewing some of the slides that Mr. Tour showed. There were two slides that showed very close relationship in the carbon monoxide, but the carbon dioxide values differed widely. That difference might be accounted for in the different percentage of total hydrogen in the original gas.

I mentioned nitrogen as being present. Nitrogen is frequently assumed to be a neutral gas in many cases where it is quite active chemically. It is well known that nitrogen is reactive with at least two of the constituents of high speed steel, chromium and vanadium.

There may be a question as to the intensity of any action between nitrogen and iron at those temperatures, but that would require further investigation to throw any light upon it.

Mr. Thum laid some stress on gradients, and led me to believe that he considered the composition gradients in high speed steel negligible.

I should like to call attention to some of the statements that were made in the book, which Mr. Thum quoted of Grossmann and Bain (p. 115) to the effect that especially in the original ingot composition gradients of ingots are quite prominent, and likewise in some of the larger sections which fabricators of high speed steel are obliged to use, where there is not a great deal of reduction from the ingots.

I have no direct evidence of this, but I can offer indirect evidence on observations of hardened and drawn pieces where the drawing has been done at a critical degree, where certain areas will show the effect of much more drawing than others when you know that the actual drawing temperature has been the same throughout. Regions in the vicinity of carbide clusters have often shown structures that were not found in adjoining spots. I suggest that that indicates very clearly strong composition gradients.

I concur with Mr. Thum that composition gradients, among other gradients, will be found to account for some of the things which have been noticed. I might also add that in an extremely fine hardness measurement which I have been fortunate to have at my command, something approaching the nature of the micro-character, although using somewhat heavier loads, we find hardness variations in which you might assume was uniform material; in terms of Vickers hardness they might vary from 700 to 900.

This I consider further evidence of composition gradients.

E. C. Bain[3]: I was in the room and heard the very interesting discussion of Mr. Tour's paper. While you no doubt realize that I cannot possibly pass judgment on such an important matter with only a few minutes' thought, yet I cannot resist the opportunity to say a few words.

In the first place, it seems to me that we are indebted to Mr. Tour for

[3]Research metallurgist, U. S. Steel Corp. Laboratories, Kearny, N. J.

giving simple, direct, concise and conclusive demonstrations of the effect of the furnace atmosphere, which is certainly an extremely important practical matter. I think we are likewise indebted to Mr. Thum for the extremely thoughtful and searching inquiry that he made into these results. As I see it, there is nothing whatever in Mr. Thum's comments to detract from the obvious importance of Mr. Tour's developments.

The only real point of difference is the identity of that black-etching constituent. All I can do is to tell you what I believe. You will, of course, expect me to be prejudiced in favor of what we said in our book.

In heating in the presence of oxygen at high temperatures, it appears that one of the most important reactions taking place is coalescence of carbide into comparatively large bits, most of them being found in the grain boundaries. Occasionally large carbide particles will be found inside the grains. I believe that the microstructure carries its own proof of one of the circumstances. You will recall that around the carbide particle (illustrates) was a little region which did not develop the black etching material and that it was normally austenite before quenching and partially martensitic after quenching.

I take it, then, that it cannot be depletion in carbon that caused this little region to remain light-etching; rather it is because it is high in carbon.

This material, which could not have had more than 0.10 or 0.15 per cent carbon when we started to heat it has only increased in carbon up to 0.25 per cent or in that general vicinity, and therefore is not able to withstand the tendency for the precipitation of high temperature ferrite or delta iron so that we have a little delta iron formed there. That, after all, seems to me to be extremely unimportant in this broad consideration. The fact is that Mr. Tour found very much more of the constituent which you are all well aware is eutectic, the herringbone structure with parallel lines. There was more of that constituent when the material was heated in the atmosphere rich in oxygen. I think we can perhaps interpret that by considering that there is a change in composition, and we can make such an assumption for perhaps two reasons:

1. That just below the critical point or below the fusion temperature there seems, in all metals, to be an extremely high rate of diffusivity of the elements, and we have noticed in carbon steels that below such temperatures the presence of oxygen seems to increase the rate of carbon diffusivity.

2. When scaling takes place we can safely say that we reduce the amount of chromium; we also reduce the amount of iron, in which we are not interested since we have an excess of iron. But tungsten is not much diminished by scaling. Therefore, if we assume that there is a change in composition, it is in the direction of losing carbon and chromium.

When we drew the diagrams for the book, we were not aware of one circumstance which now looks probable, and that is that our eutectic horizontal is not truly horizontal due to the fact that there are three or four components that we have not considered in high speed steel—that it is a sloping line, and not only that but it is a double line. If it slopes up with increasing carbon, then we have an explanation for all the phenomena, a decrease in carbon making a lower eutectic point, causing more eutectic to form with an apparent lowering of the melting point, and at the same time we may agree that this constituent is

dark-etching because of a transient rejection of high temperature ferrite or delta iron.

Let me emphasize again my view that the identity of that black-etching constituent is a rather unimportant point relative to the other features which were brought out so clearly in Mr. Tour's work.

Author's Closure

Mr. Thum's very able study of the paper was gratifying. I would rather leave this controversy between my interpretation of Grossmann's and Bain's book and his interpretation of the book for Grossmann and Bain themselves to answer.

Irrespective of the theoretical explanation of these micrographs which I have shown, the fact still remains that for practical heat treating of high speed steel, grain growth, eutectic formation, scaling, are all dependent upon the furnace atmosphere, and it is not just a simple neutral atmosphere as we ordinarily think of it that is required, but it is an atmosphere very high in carbon monoxide, the amount of carbon monoxide depending upon the temperature.

Mr. Sadtler's remarks about hydrogen water vapor, etc., are very much to the point. Water vapor of course is always present in combusted gas atmosphere. Just how much is present is very difficult to tell. When samples for gas analysis are taken, condensation in the sample tube always occurs.

It is difficult to say how much hydrogen or methane is present in a combusted gas. Analysis of the gas at room temperature, does not show what the gas mixture was at 2400 degrees Fahr. It cannot be analyzed at 2400 degrees Fahr.; what happens during cooling is not known.

I can say that in the Hayes furnace we have used we have attempted to find hydrogen and methane, and have not been able to find them in these furnace atmospheres. I think that is explainable by the construction of the furnace and the rate of burning of hydrogen. As far as methane is concerned, we know that it is entirely unstable at 2400 degrees Fahr., and we would not expect to find it anyway.

Mr. Keshian's remarks were also very much to the point. We did not place thermocouples in any of the work.

I would like to call your attention to Jominy's work at the University of Michigan, published a year or so ago, on forging steels, where he found, with thermocouples inserted in the specimens, that self-heating was not an important item on plain carbon steels until you reach 2500 degrees Fahr. or higher. On high speed steel, which does not scale so rapidly, you would not expect self-heating even at 2500 degrees Fahr. However, we did not go that high. We only went to 2400 degrees Fahr.

Jominy found self-heating only when he had oxygen present but we found rapid grain growth with carbon monoxide present.

DEVELOPMENT AND APPLICATION OF MACROETCHING

By H. G. Keshian

Abstract

The author briefly reviews the development of etching iron and steel from early days to the present time. He points out some of the principal reasons for the unusual popularity as well as the adverse criticism of the method and refers to the general effect of macroetching on the quality of tool steels of today.

Suggestions are made to more closely follow the recommended practice on macroetching by the American Society for Steel Treating and to establish graded standards for some of the principal types of etch structures. A number of photographs are given illustrating this point.

MACROETCHING has been applied to the inspection of iron and steel only recently; but as a potential testing method it antedates many other methods now in use. It was used by Reaumur (1683-1757), who in his work gives sketches of macro-etched pieces of steel, discusses macrostructure and gives directions how to distinguish by macroetching various grades of steel. Sven Rinmann, before 1774, published in Sweden a book *On the Etching of Iron and Steel* which in 1774 was translated and published in Germany, in which he says "etching gives an easy means of distinguishing between various kinds of iron and steel, as far as their hardness, density and similar and dissimilar properties are concerned".[1]

Macroetching was also used by Bergman in 1783. According to Osmond, Widmanstätten, in 1808, used acid etching to show the structure of meteoric iron.[2] Sefström, who carried out some tests with the method in 1825, says "for distinguishing the uniform texture of bar iron, this etching or corrosion with acids is a good method".[3]

[1]M. G. Yatsevitch, "The Macroexamination of Steel," *Army Ordnance*, Vol. XI, 1931, p. 297.

[2]F. Osmond, "Crystallographie du Fer," Paris, 1900, p. 25.

[3]*Jernkontorets Annaler*, 1825, p. 155.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author is a member of the society and is metallurgist for the Chase Companies, Inc., Waterbury, Conn. Manuscript received June 20, 1932.

After the experiments of Sefström with etching until Sorby's work in 1887, nothing of importance appears to have been done in this line of testing. It may be that the advent of the microscope into the study of metals during this period diverted the attention of the scientist from this subject. In 1864 Sorby in England applied the microscope to the study of meteoric and puddled iron and steel and as it is well known, in 1883, he discovered, with the microscope, pearlite in steel. In 1887 he presented his paper "On the Microscopical Structure of Iron and Steel,"[4] to the British Iron and Steel Institute, in which he also dealt with macroetching of iron, cemented steels and steels of different carbon content. He polished his samples roughly and etched them with "a moderately strong solution of nitric acid." Then he made from them what he termed "Nature Prints." He describes the procedure as follows: "In preparing the blocks used for nature printing, the specimens were cut type-height, one side made flat and roughly polished, and then sufficiently well bitten with moderately strong acid to enable me to print with ink as from a wood block."[5]

The principal object of Sorby's paper was the study of microscopic constituents of iron and steel. Consequently it stimulated the furtherance of the microscopic more than the macroscopic method. A little later Osmond's work in France and Marten's in Germany, with the microscope, apparently had the similar effect in slowing down the progress of macroetching. But the appearance of a new factor during this time obviously brought the macroetching to the forefront again. This factor was the introduction of new methods in physical testing.

Between 1860 and 1900 great changes took place in the methods for testing the physical properties of steel: so that Emery's tensile testing machine appeared in 1875. Martel introduced his indentation hardness tester with a falling weight in 1895, followed by Brinell's hardness tester in 1900 and Shore's in 1901. Barba's impact test in 1900 was followed by Charpy, Izod and Fremont impact and Stanton's repeated impact testers. The most significant fact brought out by these new testing methods was a lack of uniformity in the physical properties of steels otherwise uniform in chemical composition and heat treatment. This called the attention of the

[4]H. C. Sorby, Iron and Steel Institute, Vol. I, 1887, p. 255.

[5]Ibid. p. 259.

investigators to the inadequacy of chemical composition alone to secure material of uniform physical properties and thus emphasized the important part which the structure plays in the development of these properties.

This fact, as it was to be expected, tended to increase the use of the microscope and in the meantime created a new and larger interest in macroetching; but the momentum gained by the former method pushed aside macroetching and retarded its progress and the work started more than 100 years ago by Reaumur and Rinmann and partly revived by Sorby in 1887 and Wedding in 1889, did not gain much ground until the beginning of the twentieth century.

Heyn in 1906 using copper ammonium chloride in water as an etching reagent gave a fresh start to macroetching. Between 1914 and 1918 noteworthy work was done by Rosenhain and Haughton, Stead, Le Chatelier and Le Moine, Oberhoffer, Fry and others. All used copper chloride as a base with additions of hydrochloric acid, stannous chloride, magnesium chloride, ferric chloride and alcohol.

The year of 1918 marks an unmistakable step in the development of macroetching when Humfrey presented a paper[6] on "Macro-etching and Macro-printing." His etching reagent consisted of a mixture of copper ammonium chloride and hydrochloric acid in water. Humfrey had used the method extensively for the inspection of ordnance materials during the World War. His paper aroused great interest and the method almost instantly gained general approval.

During the same year Waring and Hofammann in America presented to the American Society for Testing Materials a paper on "Hot Acid Etching Rails and Forgings."[7] This paper should be considered another distinct advance in the development of macroetching for more than one reason.

Up to this time all etching reagents used belonged to, what we may call weak acids, and were used cold, generally giving a shallow etch. The specimens to be etched required quite finely polished surface and close attention in handling. On the other hand Waring and Hofammann's reagent consisted of a strong combination of nine parts of hydrochloric acid, three parts sulphuric acid and one part

[6] J. C. Humfrey, *Journal*, British Iron and Steel Institute, Vol. 99, 1919, p. 273.

[7] F. M. Waring and K. E. Hofammann, *Proceedings*, American Society for Testing Materials, Vol. 19, II, 1919, p. 182.

of water. They produced a deeply etched structure and their results were excellent. From then on application of macroetching gained great popularity and since then almost a new branch of literature on macroetching has developed. The industrial application of the method as a means of examination and inspection has been so wide that some of the technical societies here and abroad have devoted special attention to it. Among these societies may be mentioned the Society of Swedish Metallographers for their "Metallographers' Handbook of Etching,"[8] American Society for Testing Materials and American Society for Steel Treating for their recommended practices for macroetching.

II. Two Interesting Aspects of the Method

When considering the development of macroetching two peculiar but interesting phenomena become evident. *First*—an unusual rapidity with which the method has gained general application during the last several years. *Second*—an intense discussion of the method, mostly of adverse nature by the seller, which has not been the case with the average testing method.

Some of the principal reasons for the quick popularity of macroetching appear to be as follows:

(a) The relative simplicity with which macroetching can be made, requiring only simple equipment and easily acquired technique for the actual routine of carrying out the test.

(b) Many serious defects when present in steel can be revealed quite forcibly with macroetching. So that when macroetching was being given considerable attention (about 1919), there was a large accumulation of steel that was manufactured under abnormal conditions of the World War. The application of macroetching to these steels disclosed much poor material and thereby it enhanced the merits of macroetching as a valuable method of inspection. Again, macroetching as a method for disclosing the inner defects of steel, is definitely wider in its scope than many other methods used for a similar purpose; because it reveals a panoramic view of as large a section of the metal as may be desired which can be seen at a glance. In this respect it is vastly different from fracture and microscopic methods.

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[8]T. Berglund, "Metallographers' Handbook of Etching," Sir Isaac Pitman & Sons, London. 1931.

Macroetching also has the advantages of a nondestructive method of test. A typical example of this feature is the case where a piece of steel can be examined in this manner to reasonably assure its freedom from serious defects before such steel is made into costly tools.

The other aspect, namely, the adverse criticism to the method still present in some quarters, it must be admitted, cannot be explained entirely by the seller's opposition often shown to inspection methods. There are, indeed, also other reasons.

Macroetching, like other testing methods, requires certain essential knowledge and definite procedure for its successful functioning. *First*—it must be carried out under standard conditions, as regards the preparation of test pieces, the etching reagent, time and temperature of etching, etc. *Second*—it must be done with sufficient knowledge of the fundamental factors underlying the manufacture of iron and steel. *Third*—the decision in accepting or rejecting the material thus tested must be made by necessary experience with the operations or the mechanical conditions under which the steel is to be used. Unfortunately, however, the widespread use of the method in its early stages was so rapid that at that time there existed neither a standard procedure of etching nor the essential knowledge on the part of some who used the method. This resulted in some abuse which together with the usual disturbing effects of a new testing method created an undesirable situation.

III. Macroetching at Present

The conditions surrounding this method, however, have now changed considerably, and it is being used extensively in this country and abroad by many steel mills as well as by consumers. The net result has been constructive. Unquestionably the standard of quality of tool steel of today has been raised and the macroetching has played no mean part in this progress. Furthermore, its effect has been to enrich the existing knowledge of the nature of steel and has made the consumer more familiar with the problems of the steel maker in his efforts to raise the standard of quality of his product.

The development of the method, however, is not complete yet. There are still certain problems to be worked out. Some of these will be dealt with by other contributors to this symposium, but there are two which, perhaps, should be considered here.

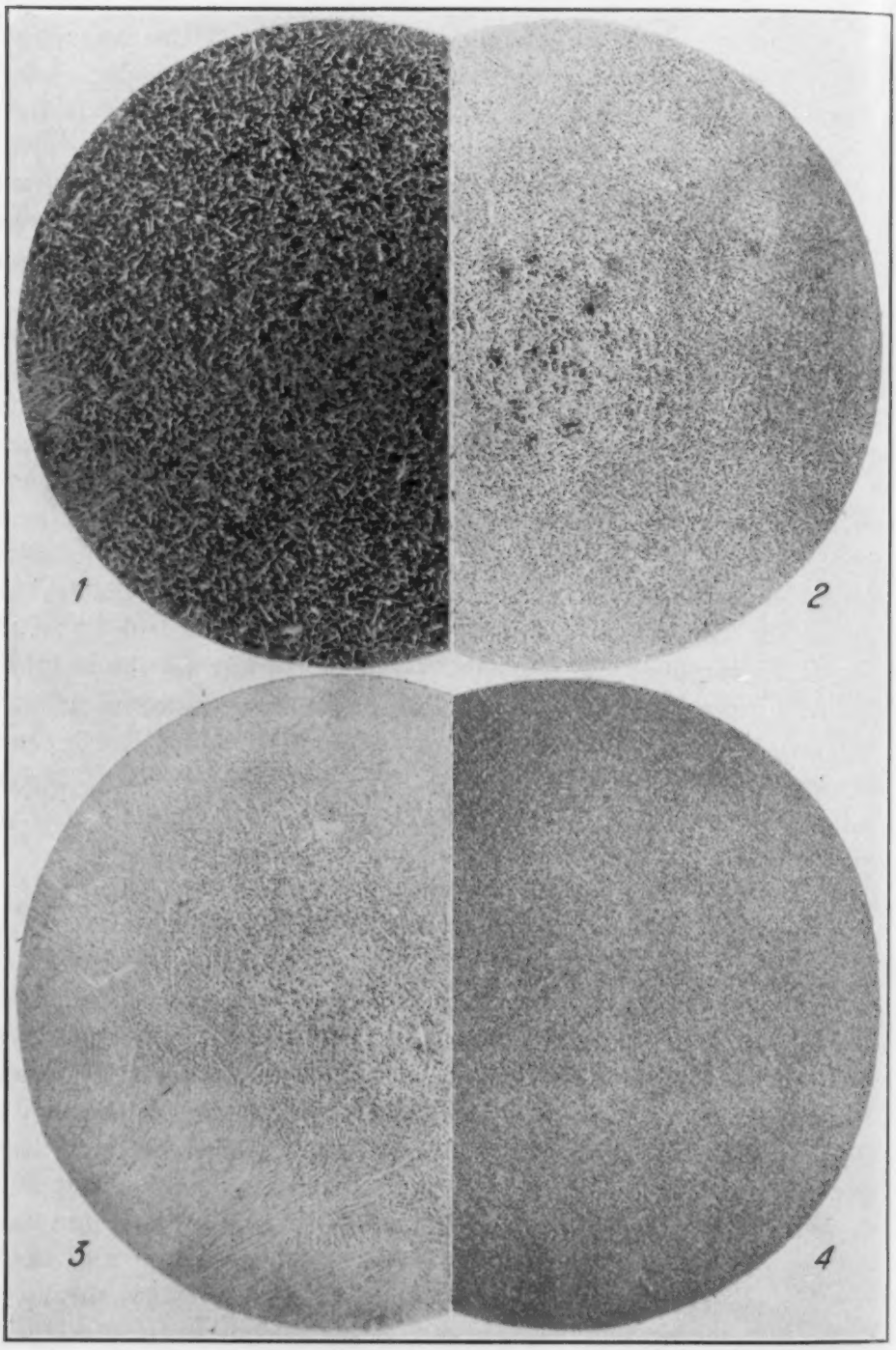
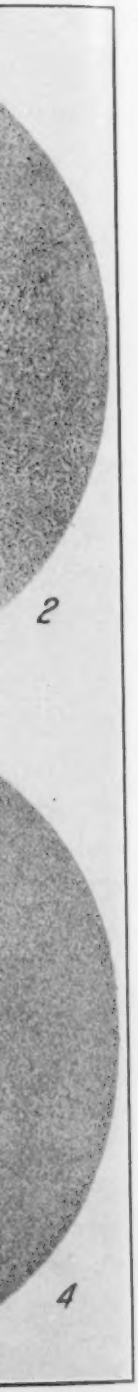


Fig. 1—Macrograph of Steel Bar which is an Example of Excessive Porosity. Fig. 2—Macrograph of a Steel Bar which Shows a Relatively Less Porous Structure than Fig. 1. Fig. 3—Macrograph of a Steel Bar Showing a Porous Structure Less Objectionable than Fig. 1 or Fig. 2. Fig. 4 is an Example of an Etched Structure Free from Porosity.



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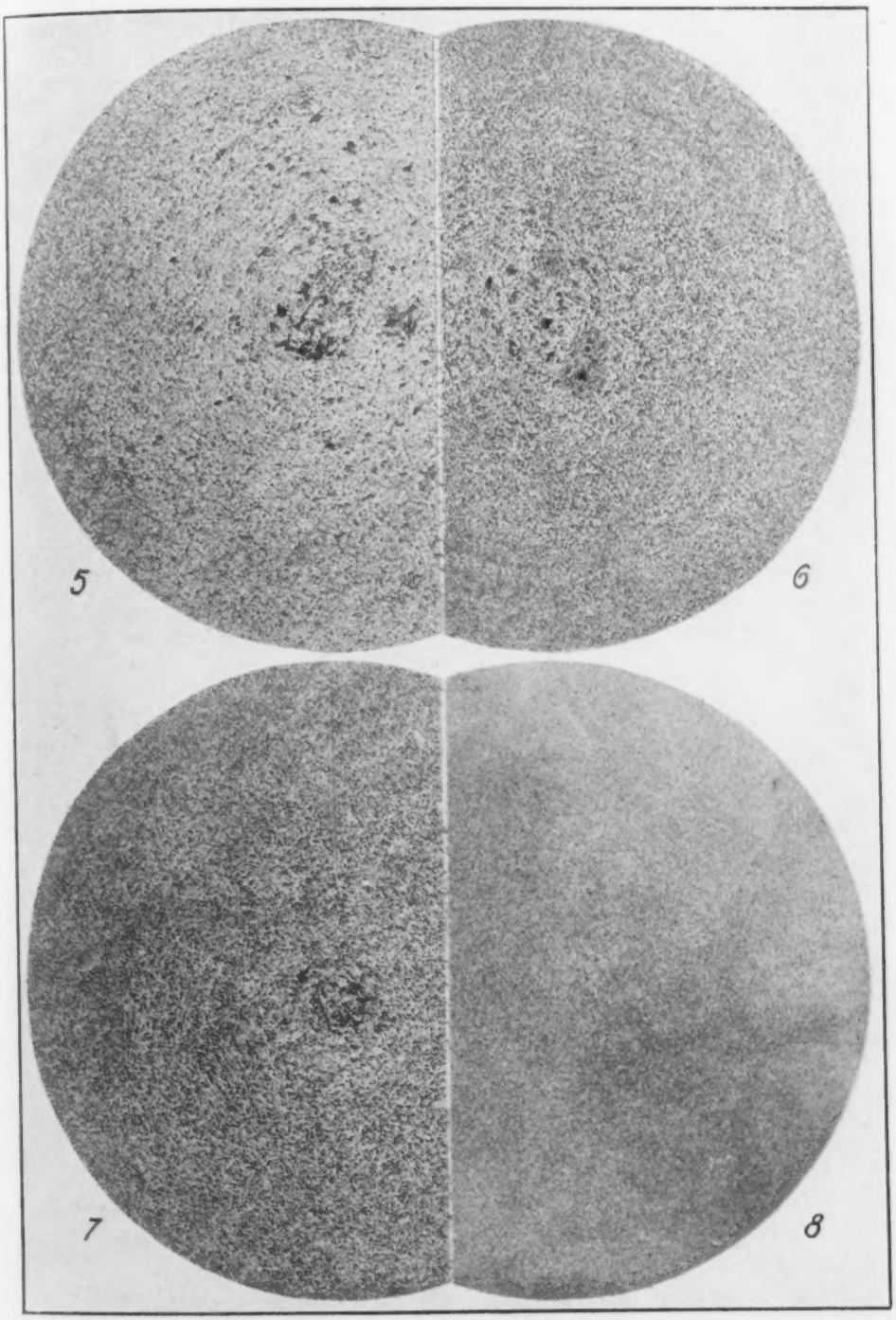


Fig. 5—Macrograph Illustrating a Serious Segregation. Fig. 6—Macrograph Showing a Relatively Less Serious Segregation than Fig. 5. Fig. 7—Macrograph of an Etched Structure Showing Slight Segregation. Fig. 8—Macrograph Showing a Structure Free from any Segregation.

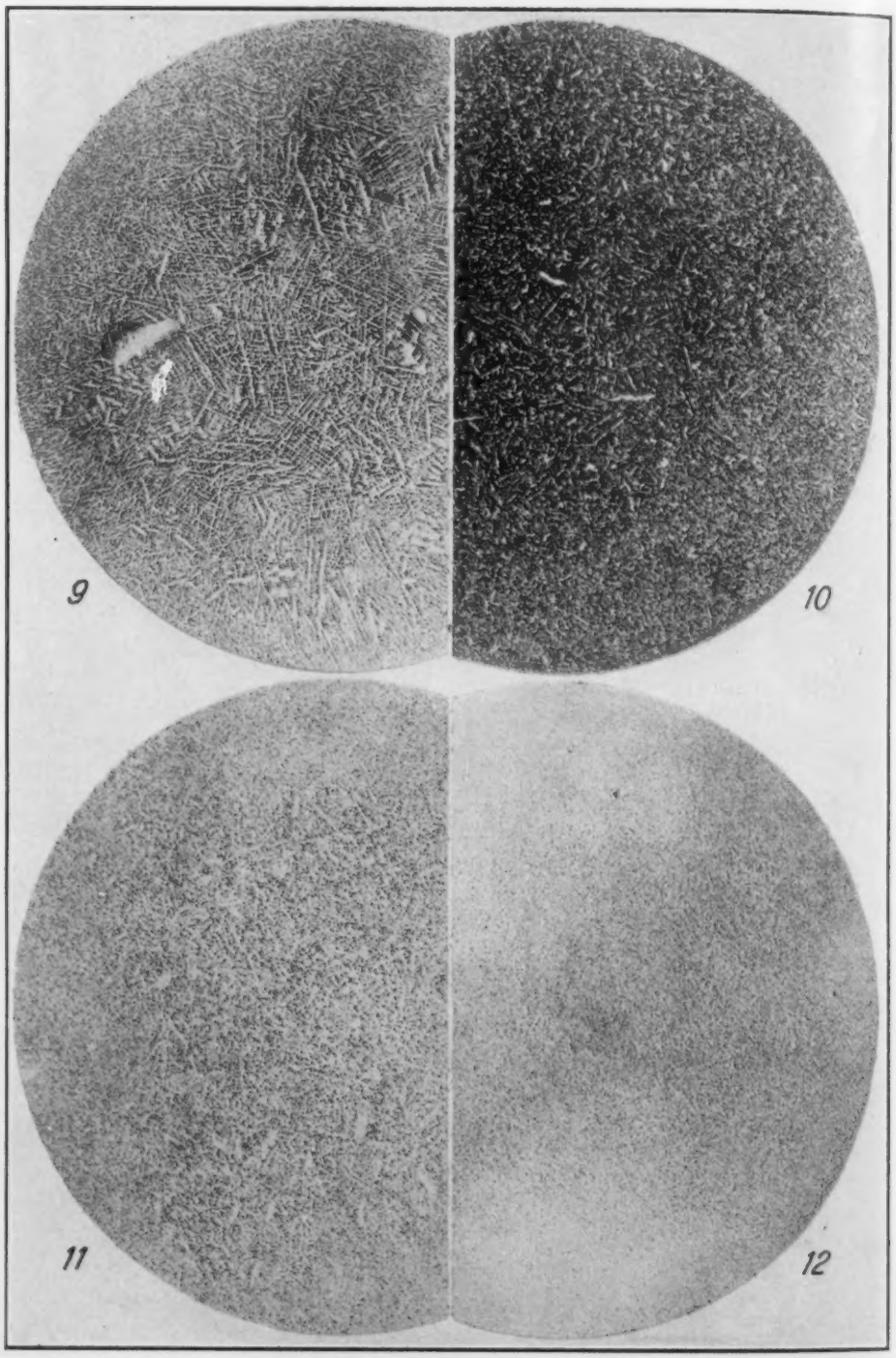


Fig. 9—Macrograph of an Etched Steel Bar which May be Considered as a Coarse Dendritic Structure Representing an Extreme Case. Fig. 10—Macrograph of a Moderately Dendritic Structure. Fig. 11—Macrograph of a Steel Bar which is an Example of Less Coarsely Dendritic Structure than Figs. 9 and 10. Fig. 12—Macrograph of a Steel Bar Showing a Structure Free from Dendrites.

(A) The importance of carrying out the etch test under standard conditions has been mentioned elsewhere; yet in spite of the general use of this method at the present time the test is frequently applied in a manner clearly showing absence of uniform conditions, both in regard to the preparation of the specimens and the time and temperature of etching. Inasmuch as the proper functioning of macroetching largely depends on these factors, it is necessary that the standard practice recommended by this Society be followed closer than it is being done now. This standard, if necessary, should be revised in the light of added knowledge since its publication and the knowledge resulting from this symposium.

(B) One of the serious problems connected with the proper application of macroetching is the difficulty to classify some of the structures revealed by etching, as a basis for acceptance or rejection.

When the etch test discloses serious defects the decision can be made, relatively easily; but where the type of structure cannot be so easily classified as decidedly good or bad, it becomes necessary to set up a series of standards showing what is acceptable and what is not. Among these types of structure may be mentioned porosity, segregation and dendritic structure.

Some such grading of porosity may be worked out like the one shown in Figs. 1 to 4. Fig. 1 represents an extremely porous structure and Fig. 2 a structure less porous and so on until we come to Fig. 4 which is free from porosity. Figs. 5 to 8 show varying degrees of segregation. Fig. 5 is an example of serious segregation, Fig. 6 less serious, and Fig. 8 free from segregation.

In Figs. 9 to 12 are shown the different degrees of dendritic structure ranging from very coarsely dendritic state to one almost free from visible dendrites.

If standards of this nature are prepared for the principal types of steel they should prove of much value, first for allocating steels of particular structure to certain application, second for bringing about a more desirable understanding between the steel mill and the consumer regarding the application of macroetching, because it often happens that a steel mill has no way of knowing just, say, what degree of porosity or dendritic condition will be acceptable and what degree will not be, to the consumer.

If standards such as these can be worked out and mutually agreed upon, many of the present difficulties arising from this source will surely be eliminated.

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DISCUSSION

Written Discussion: By Dr. H. S. Rawdon, Chief, division of metallurgy, U. S. Bureau of Standards, Washington, D. C.

The author's resumé of the historical aspects of the macroetching method is of decided interest. It is the writer's opinion, however, that such a resumé has considerable value in addition to the mere interest it excites. No thoughtful worker can help being impressed and stimulated when he considers that the method which he is using has stood the test of time for a century and a half, as is the case here. It is somewhat akin to the thrill which one experiences when he sees and handles the tools and materials used by a pioneer worker in any line, as for example, the actual specimens used by Sorby in his notable work in metallography.

The uninformed reader may perhaps form the impression in reading this paper that the field of application of the macroetching method is a much more limited one than is actually the case.

In the writer's opinion, the author has not stressed sufficiently the practical application and inherent possibilities of the method aside from those which most closely touch his particular line of activity. The methods used by Stead, Fry, Rosenhain and other workers which depend on the use of an acid solution containing copper in some form is still of great practical importance for studying the distribution of phosphorus and other impurities as in the banding of steel. Other copper solutions are of very great value in the insight they give us as to the internal condition in strained low carbon steels. While the method in this particular form has not reached the stage of being employed as a routine test, its value in investigative work on defective and failed materials as well as for research purposes is undisputed. The use of macroetching for wrought iron, the first application, still continues to constitute one of the decisive tests included in all specifications for this material. Nor is the macroetching method confined to steel and iron. It is extensively used in the aluminum and brass industries. The practice of etching duralumin airplane propellers at regular stated intervals for evidence of incipient failures is a good example of the importance attached to the method in this industry. Numerous other examples might be cited to emphasize the point that the field of application of macroetching is an exceedingly broad one.

While it is recognized that the need for close control of the conditions of testing is not so vital as is the case in some other lines of metal testing, the author's plea for standardization of conditions for macroetching has the full support of the writer. The very simplicity of the method may often mitigate against the value of the results obtained. Until one has had considerable experience in this line of work and has a good general knowledge of the material with which he is working, careful consideration should be given to the details of its application. Especially in the case of acceptance tests of materials based upon the macroetching method should the details of the testing methods be carefully and scrupulously controlled.

Written Discussion: By W. H. Wills, metallurgist, Ludlum Steel Co., Dunkirk, N. Y.

Macroetching or deep acid etching has become increasingly important in

recent years as a method of testing tool and special alloy steels for internal and in some cases surface defects. It is applied mostly to annealed bar stock. Our records over a period of almost 3 years show of the routine tests going through the physical laboratory 15.5 per cent are deep etch tests representing about 300 tests per month. Of material thus tested rejections run about 5 per cent.

It is important that the test on a given grade of steel be carried out under standard conditions and the use of 1:1 HCl following the method recommended in the A.S.S.T. Handbook seems to be quite general.

The basis of acceptance or rejection is indefinite in some cases except of course when pronounced defects show up. It is difficult to set up general standards of center porosity due to the variety of applications to which the steel is put. For instance rounds of carbon tool steel for cold header, embossing or drawing dies where the center is subject to wear would be subject to a higher standard of center porosity than flats going into blanking or open cold header dies. This problem can best be worked out by close co-operation of the mill and user.

Mr. Keshian states that macroetching has the advantage of being a non-destructive method of testing. We do not think that this is generally the case. Testing bar stock means that a disk must be sawed, which after etching is scrapped unless used for micro examination or other physical tests. Pieces handled in the etching bath must be comparatively small and even if for instance an entire piece of tool steel for an intricate die were deep etched it would be necessary to remove material representing the maximum depth of penetration of the acid.

Written Discussion: By C. C. Henning, metallurgist, Pittsburgh Works, Jones and Laughlin Steel Corporation, Pittsburgh.

Mr. Keshian's suggestion for the adoption of a standard etch test in general steel specifications presents the subject in a clear and logical manner.

He has correctly made the point that the etch test is a discriminating test revealing another sidelight of steel not covered by other testing methods. As such, it will undoubtedly involve the rejection of some appreciable tonnages if generally applied. The first question which requires answer then, is the economic justification for the test. Will such a test become a greater economic burden to producers and consumers than the benefits that can be obtained by it? What are the extents of the burden and the benefits?

Under his listing of reasons for adverse criticisms is stated—"It (the etch test) must be done with sufficient knowledge of fundamental factors underlying the manufacture of iron and steel." This is a large order and we venture the thought that only a minor percentage of the persons into whose hands the etch test would go for execution would properly qualify as having sufficient knowledge to evaluate and discriminate among the varied etch patterns presented for his inspection. On this basis alone, it is almost certain that a great deal of steel would be rejected that should amply qualify for the application involved.

Again it is stated—"The decision in accepting or rejecting the material thus tested must be made by necessary experience with the operations or the mechanical conditions under which the steel is to be used." This presupposes a detailed knowledge by the inspector, of fabricating and service conditions and sufficient judgment and ability to correlate the effect on these, with each detail

of etch pattern presented. The qualifications are high and no doubt even with such high qualifications impartial decisions will be made because on the inspector's part will be the natural incentive and tendency to apply generous margins of safety in his decisions at the expense of the steel supplier.

In our opinion the macroetch test has merit and may be justifiably resorted to:

(1) As an acceptance test for the determination of clearly recognizable and nondebatable features such as seams, pipe, excessive segregation, surface and internal cracks, and mechanical defects.

(2) As an informative test to be correlated with other tests, fabricating operations and service life for further information and development of steel quality.

Written Discussion: By James J. Curran, 1843 No. Stanley St., New Britain, Conn.

Having been identified with the earliest application of deep etching, as now practiced, to structural and tool steels, the writer is keenly interested in the papers on this subject to be presented at this convention. Of these, a preprint of the paper by Mr. Keshian, and an abstract of the paper by Messrs. Gill and Johnstin have come to hand.

Both papers are cautionary in nature. Mr. Keshian notes that the quality of tool steel has improved greatly, since, and as a result of, the development of the deep etch, but emphasizes the necessity for strict adherence to standard methods, and points out difficulties in interpreting and classifying border-line and questionable structures encountered. Messrs. Gill and Johnstin illustrate the effects of different reagents, and point out the failure of the most commonly used reagent when applied to some special steels and to some conditions of heat treatment.

It is unfortunate that to many, the warnings in these papers will take on undue emphasis, and tend to discredit the test. Actually, these departures from the normal merely go to indicate that deep etching is not a closed book, nor is it any more fool-proof than other methods of metallurgical investigation. It is a fact that it is one of the simplest tests available, and furnishes a maximum of information with a minimum of effort. If applied in a common-sense manner, with a reasonable knowledge of the methods of manufacture of steel, and the uses to which it is to be put, there is little reason to be apprehensive of the results obtained.

Standardization of all testing methods is desirable, even though it entails compromise. But the adoption of standards should not be permitted to stifle progress. The paper by Messrs. Gill and Johnstin, while an argument for standardization, is at the same time conclusive proof of the need for flexibility, and emphasizes the need for further investigation into reagents for special steels and the various heat treated conditions.

Written Discussion: By R. E. Christin, metallurgist, Columbus Bolt Works Company, Columbus, Ohio.

A consumer of tool steels, in particular, cannot avoid interest in the author's paper. For omitting analyses of the steels used on tools and dies, Mr. Keshian must expect criticism. No technical report of tool steels could be complete without the full story of the nature of the steel.

On the other hand, what really counts in the selection of the proper grade of tool steel is the result. Through experience, the author has confirmed his stand on what method of testing is really essential in the final adoption of certain brands of steels which will give performance.

In the application of 0.95 per cent carbon tool steels to cold header dies, the writer began in 1924 with tools which failed to give average results in service. These tools when macroetched, disclosed the origin of failure to be defects, such as internal seams, inclusions, segregation, etc. Checking these defects under the microscope proved that the deep etch test (which has been written since as a standard procedure in the A.S.S.T. Handbook) was a quick and reliable method of attack to detect causes of failures, thereby eliminating one variable, at least.

It is only natural that the manufacturer of tool steels would oppose the general use of macroetch for the basis of rejection or approval of tool steels to be used in expensive dies. The writer has applied this test for eight years and today we must admit that the quality of tool steels for cold heading and trimming dies has increased to a considerable extent. Although the manufacturer offered considerable opposition at first, the co-operation now being received is highly commendable. Any new method of inspection is questioned at first but gradually the demand for better steels is answered by the "man at the mill."

Mr. Keshian has shown courage to challenge the manufacturer on the latter's own methods for detecting defects and is to be congratulated even though he has omitted an essential part—the analysis of the steel.

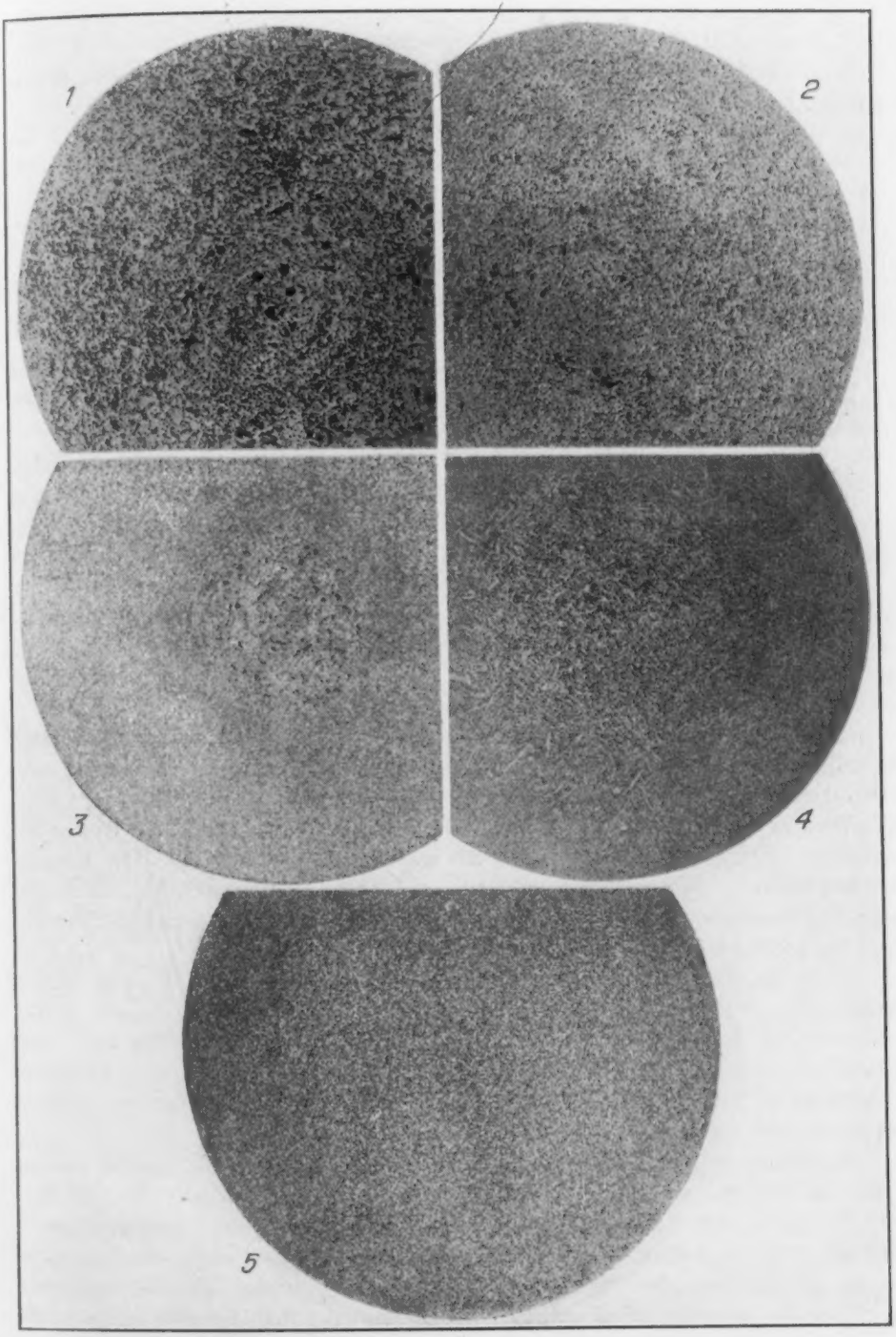
Written Discussion: By G. Lofberg, vice-president, Uddeholm Co. of America, New York City.

Originally we used for porosity testing reagent a solution of 10 per cent sulphuric acid, at room temperature, in which the test pieces were immersed for a period of 24 hours. As is apparent, however, this was a very slow process, and furthermore did not yield uniform results.

We therefore found it necessary to seek new reagents by extensive experimentation, and finally adopted hydrochloric acid as the most ideal. Our original solution had a concentration of 23 per cent, which was adapted for its particular stability, as it remained constant at this concentration up to and during boiling. Whenever we used weaker solutions the concentration increased with higher temperatures, whereas stronger solutions decreased, until the stability level around 23 per cent hydrochloric concentration was inevitably reached.

However, we were not satisfied with the uniformity of etching obtained and by extended experimentations finally adopted our present standard, which stands as follows: Hydrochloric acid of about 14 per cent concentration at boiling point for 15 minutes.

Preparation of samples. The steel for investigation is annealed before testing in case of carbon steels of 0.50 to 0.85 per cent carbon at approximately 1380 degrees Fahr. and for carbon steels of 0.85 and higher carbon at 1400 degrees Fahr. We use normally one hour for thorough heating at these temperatures and comparatively rapid cooling in the furnace. From the annealed steel, we then cut the disks which are planed to approximately 3/8 inch thickness, coarse ground on one side, and washed in ether.



Figs. 1 to 5—Deep Etched Disks Showing Five Degrees of Excellence of Specimens. These Have Been Established as Standards.

Etching procedure. The above mentioned solution (about 14 per cent hydrochloric) is obtained by adding one part water to one part concentrated technical hydrochloric acid, containing about 28 per cent hydrochloric, specific gravity 1.19.

This solution is heated in a lead container until boiling commences. The disks are then immersed, ground surface up. They are allowed to remain until the solution resumes boiling, and from this moment 15 minutes more. It is a strict rule that results must not be jeopardized by crowding. Thus no more disks are etched at any one time than can conveniently be placed on the bottom of the container, permitting complete exposure to the reagent of the entire surface of every disk involved. Furthermore, the etching reagent must never be used for more than one etching.

Cleaning. The samples are now washed in water and then in alcohol. They are dried in a warm place and slightly oiled with machine oil while still lukewarm.

Standards. The standards we go by are better illustrated by the attached five (5) photographs showing excellence as represented by standard No. 5 and uniformly stepped down to No. 1. For practical operation the standard is reduced to three, numbers 3, 4 and 5.

H. T. MORTON:[1] We have been etch testing tool steels for a number of years. Cold header dies are probably the most important where you need a steel with a very good center, free from nonmetallic inclusions. On certain tool steels where the center is cut out, you can use a more porous center but such things are in the hands of the plant metallurgist.

If there is proper co-operation between the plant metallurgist and the steel metallurgist, the etch test should be no hardship on the steel company and should give a quality of steel that will be very satisfactory for tools.

Similar difficulties have arisen with stainless steels. There you must eliminate segregates as well as various impurities in the steel. The simplest method seems to be a proper etch test by disk inspection of each bar. With this material there should also be proper co-operation between the steel metallurgist and the plant metallurgist.

HAAKON STYRI:[2] I have read Mr. Keshian's paper carefully and with a great deal of interest and would like to call your attention to some of the requirements for proper etching, namely: standard conditions for etch, sufficient knowledge of steel manufacture and necessary experience with operating conditions of the steel, and, I will add, knowledge of relation between etching structure and performance of steel.

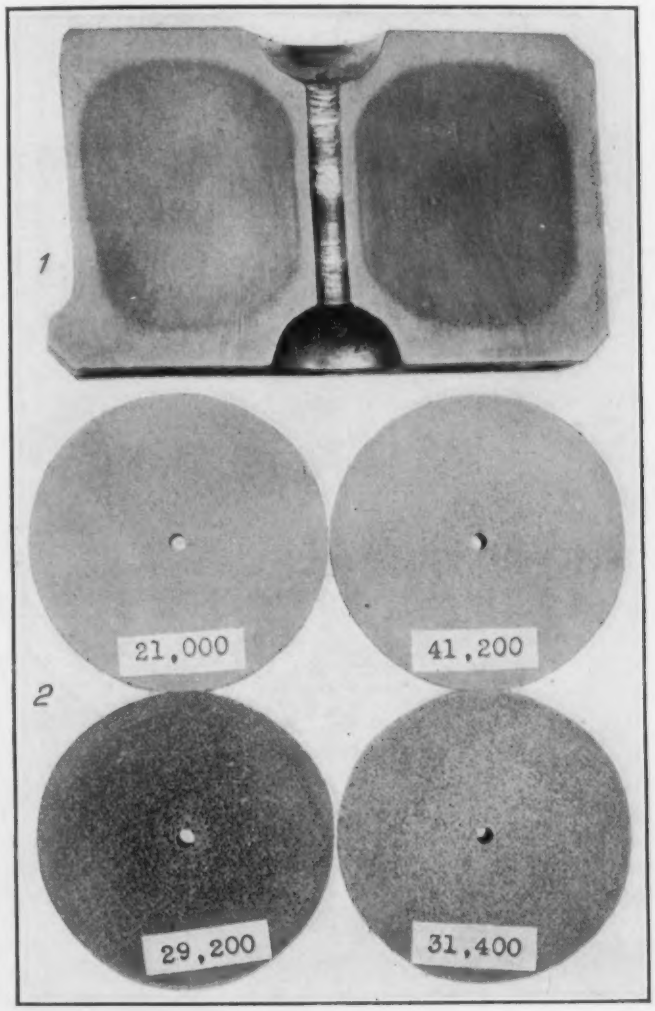
Referring to Mr. Keshian's pictures and description, one should assume that the material giving the most pronounced ingot structure, for instance, Fig. 9, should not be satisfactory in ordinary production but I believe it justified to ask for test data which should tell in what respects such structure gives poorer results than, for instance, Fig. 12. I also consider Mr. Keshian's use of the word "porosity' in describing Figs. 1-4, misleading, because he refers to

[1]Metallurgist, Hoover Steel Ball Co., Ann Arbor, Mich.

[2]Director of Research, S K F Industries, Philadelphia.

the surface condition of the disks produced in etching. A more proper name would be "etching pits." If microstructures of such disks had been studied I think in the majority of cases the sample would be found free from porosity.

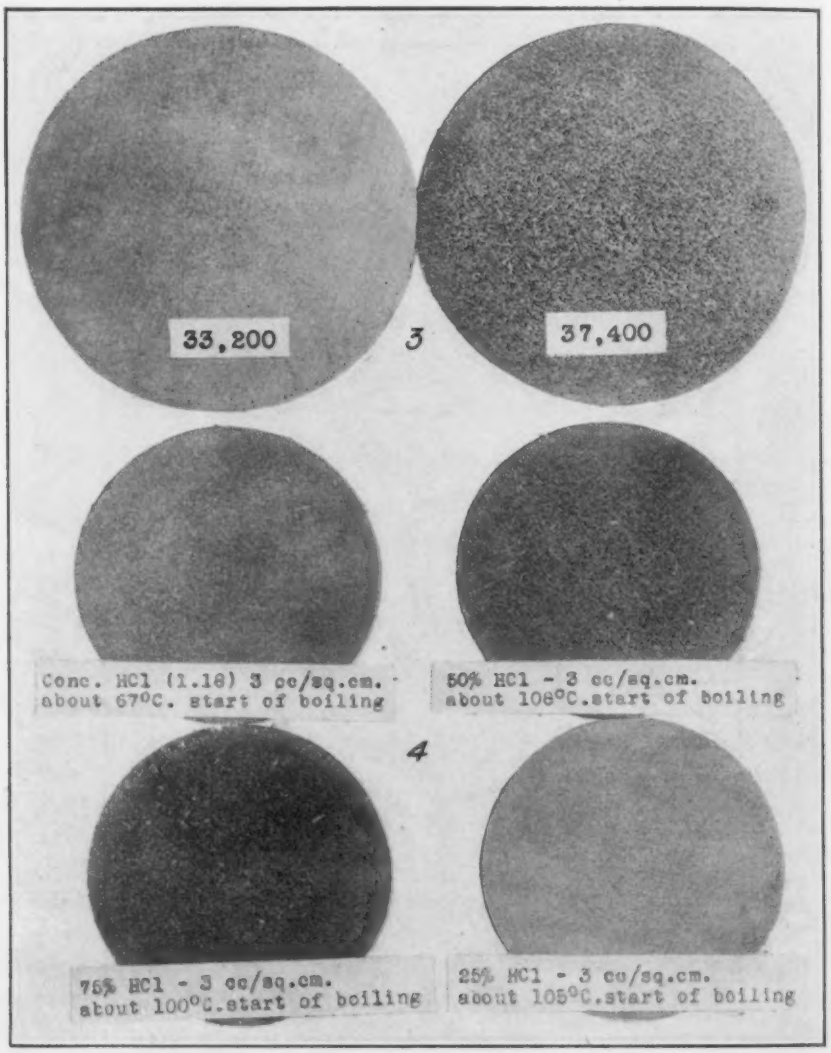
While the great usefulness of deep etching is freely admitted, too often an arbitrary stand is taken, that certain etching structures show defective material, without any investigation of relation to production.



To illustrate more in detail what I am aiming at I refer to some figures of production of cold heading dies of the type shown in section in Fig. 1. The die is water-hardened from 1600 degrees Fahr. in a fixture with controlled spray playing into the ball cavities.

Fig. 2 shows four disks taken from dies annealed after failure with production as shown and the steels are from four different manufacturers. The dies were etched with 1:1 hot hydrochloric acid, and it will be seen that the steel with the best etching structure has the lowest production while the highest pro-

duction gives a surface pretty nearly as good. On the other hand, the die which gives mean value and which is representative for average die production shows decidedly poor etching. The disk that gave 31,400 balls etched a little better. Examined by the microscope this last disk showed the greatest slag content while the first disk was the cleanest and the other two intermediate.



Disks shown in Fig. 3 were taken from bar stock from which dies with indicated production were made. Here the poorest structure was of the steel that gave the highest production whereas the die that gave very good etching had the lowest production. These samples are not shown to indicate that a steel with poor etching should be preferred to a steel with fine etching but to point out that it is not in general justified to condemn a steel due to segregation or numerous etching pits, because these have little or no relation to the quality of the material as judged by its performance.

It is further of interest to point out the importance of proper procedure in etching in order to get comparative results. For this purpose Fig. 4 shows disks taken from the same bar adjacent to each other, surface ground and etched for the same time in different concentrations of acid. You will see that we can obtain almost any character of deep etching we want by various procedure in etching. A standard for etching for each kind of steel must, therefore, absolutely be maintained in order to get comparative results.

It is evidently important, to use this type of etching with the greatest caution except for revealing rather obvious defects, and only when production data very definitely show certain structures developed in etching to give poor results in production should it be used as acceptance test.

G. J. Comstock:[3] I would like to say that it seems to me that in the deep acid etch we have gotten hold of tests which we cannot give up. Even here in our own society we are not entirely in accord on it, but I think we will agree that it has its merits.

There are other uses that have been brought out for the deep acid etch, or modifications of it, than those which have been discussed, such as illustrating the hardening of steel by selective etch of hardening sections.

I think that Mr. Luerssen's paper and Mr. Gill's paper have brought the fact out that the steel maker has taken up a test which at first seemed unfair because of this matter of interpretation, and is attempting to use it not only to make better steel for the customer but also to improve the separate operations of his manufacturing program.

I do not think that we can afford to discount the macroetch. I do think that if we have such excellent work on it as was demonstrated by Mr. Yatsevitch's paper, as time goes on we will learn more about the deep acid etch test, and we will all profit from it whether we are manufacturers or consumers.

There is a committee of this society which has been working on the deep acid etch, and has evolved a method of acid mixtures which, I am glad to see, is meeting with some application. It seems to me, however, that even this session brought out the point (from Yatsevitch's curves and also from work done by Gill and Luerssen) that a single acid mixture or a single time is not going to cover the ground as we had hoped.

Author's Closure

Dr. Rawdon seems to think that the paper may impress the uninformed reader that the field of application of macroetching is a limited one. But within the last several years this subject has been so extensively discussed that no detailed account of its application was again considered necessary. However, even then, the reader need not think that the macroetching has only a limited field; because, in addition to a long list of references at the end of the paper, the wide application of the method both abroad and in this country has been specially referred to in the first paragraph of page 292.

It is true that the subject of macroetching has been treated in the paper largely from the standpoint of its application to iron and steel, but this is not due to any unfamiliarity of the writer with its application to other fields, but due

[3]Director of Research, Firth-Sterling Steel Co., McKeesport, Pa.

to the fact that it is in the iron and steel industry that the method has gained its present importance and also it is in this field that the method is being used on a more commercial scale than in any other field.

Etching reagents containing copper have certainly their place of application in macroetching, and they should not be considered as superseded by other acids; but their use is confined to particular fields as Dr. Rawdon mentions. Furthermore, they lack the general utility and the convenience of application with other etching reagents, such as hydrochloric acid, have.

When a steel mill furnishes to its clients material subject to etch test without knowing in advance just the type of etch structure that would be acceptable, this at times results in complaints or rejection of the material. As an aid to overcome this difficulty it was suggested in the paper that a series of etch structures might be worked out as standard and agreed upon between the two parties.

Mr. Wills referring to that thinks that it is difficult to set up general standards for center porosity due to the variety of applications to which the steel is put, but it seems to me that that is one of the reasons that make such standards necessary from which can be picked out the structure best suited for a given operation.

Considering Mr. Wills' own example of close and open dies for cold heading work, if he knew that his client was going to use the steel for close heading die he would have furnished him bars with dense centers, but how can he be sure that what he considers sufficiently dense would also be considered sufficiently dense by the customer, without having agreed upon certain types of structures? A good way of making sure that he and his client are speaking the same language would be to prepare a series of such standards and refer to them for the degree of density desired.

I agree with Mr. Henning that now and then good material may be unnecessarily rejected by deep etching in the hands of unqualified persons; but is not the same true about other tests? At times a limited number of, say, tensile tests are considered sufficient to accept or reject a large lot of material and if rejected, very often much of the good material is also rejected in this way. Again, now and then we see the rejection of perfectly sound material because of the slight variation in chemical composition and without any direct evidence as to the adverse effect of this variation on the physical properties of the material in service. In any testing method used for acceptance this danger to reject satisfactory material is always present. In fact, even more severe criticism has been made recently of the general technical methods used in the sale and purchase of steel,[4] but I am glad that Mr. Henning in the meantime concedes the merit of deep etching and the sphere of application which he assigns to deep etching in his closing sentence is well taken, at least at the present time.

Mr. Curran considers my treatment of the subject somewhat cautionary and therefore rather a deterrent to the progress of the method. Where the etch structures, other than those which show obvious defects, are concerned, I still feel that the interpretation of such structures is not as simple as the mere

[4]H. W. Graham, "A Modern Conception of Steel Quality," a paper presented to American Iron and Steel Institute, 1932.

process of making the test itself. When we consider the number of persons now using the method without sufficient knowledge of the fundamentals of steel metallurgy, I believe Mr. Curran will agree with me that my attitude in suggesting a certain amount of care is justified and beneficial.

Mr. Christin's discussion brings forth another fine example of the practical usefulness of macroetching and I am indebted to him for his contribution, but I am sorry to have disappointed him by not including in the paper the chemical compositions of tool steels—to do that would have been outside the scope of the paper.

Mr. Lofberg's description of macroetching as practiced at the Hagfors Works of the Uddeholm Company is very interesting and is very much appreciated. It is to be noted that their series of experiments led them to the adoption of 1:1 hydrochloric acid which is the same reagent recommended by this society. Their porosity standard as illustrated by the photographs is surely another step towards a better and more intelligent use of the method.

Mr. Morton's confirmation of the merit of deep etching as applied to testing steel for cold heading dies is very gratifying and it is hoped that he will some day give us the results of his experiences with steels of various degrees of porosity as affecting the performance of cold heading dies and punches.

Dr. Styri prefers the term "etching pits" to "porosity." The word "porosity" in connection with macroetching now is generally used to denote a roughened or a non-dense structure. Whether the term "etch pit" can convey this idea better than the term "porosity," will perhaps be decided again by usage. Dr. Styri's test with steels with dense and segregated centers for header dies is interesting, but not quite convincing; because from his Fig. 2 it will be noted that contrary to his statement, steel with the best etching structure gave the highest production. Furthermore, his figures do not represent an average of a sufficient number of dies which is particularly necessary in cold heading die test. Neither has he stated the chemical compositions of the steels he has used, the hardness of each die, etc. Therefore, it is to be hoped that Dr. Styri will some day make further tests with greater detail and then perhaps his conclusions will be more convincing. Even then, however, I doubt very much that he will advocate making steels with segregated centers.

ESSENTIAL FACTORS IN CONDUCTING THE MACRO-ETCHING TEST UNDER USUAL PRACTICAL CONDITIONS OF PRODUCTION WORK

By Michael G. Yatsevitch

Abstract

This paper contains a general discussion and certain data of special experiments leading to the establishment of a standard practice for the macroetching test convenient for usual industrial conditions. The principal factors affecting the results of such a test are considered, and several etching reagents are studied comparatively. One etching reagent, surface finish of test specimens, etching time, and temperature are particularly considered from the point of view of standardization. General directions for carrying out the test on the lines of the accepted practice at the Watertown Arsenal are given. Helpful suggestions regarding the cleaning of tarnished and rusty macroetched specimens are offered, and a satisfactory and more delicate macroetching method with the use of citrates or citric acid is suggested.

FOR a considerable time a series of investigations in connection with the macroetching method of examination of steel has been conducted at the laboratories of the Watertown Arsenal, the principal purpose being its application to the production and inspection of ordnance material. Among the most important questions naturally appeared the question of selecting a standard reagent, suitable for general work, and a simple, practical, and uniform method of its use in carrying out the macroetching test for the various steels required for ordnance purposes.

In general it can be said that a macroetching test consists essentially in determining the extent and character of the nonhomogeneity of a given piece of metal. This nonhomogeneity has its cause in the chemical composition and in the conditions and character of the treatment to which the metal was subjected, and is reflected in the metallographic structure. It is revealed only because of the difference in the chemical relations between the various structural

A paper presented before the Fourteenth Annual Convention of the society, held in Buffalo, October 3 to 7, 1932. The author, a member of the society, is metallurgist, Watertown Arsenal, Watertown, Mass. Manuscript received August 22, 1932.

elements composing the metal and the selected macroetching reagent. Therefore many factors bearing on this chemical action will determine the results.

Principal Factors Affecting Macroetching

According to present knowledge, the principal factors affecting the results of the action of macroetching reagents may be classified as follows:

1. Factors pertaining to the steel specimen itself
2. Factors connected with the etching reagent
3. Factors representing the conditions under which the action of the reagent on the specimen is carried out.

Factors of the first group are:

(a) The chemical composition of the steel
(b) Its condition affecting the metallographic composition (such as cast or forged condition, character of previous heat treatment, previous cold or hot working of the metal, etc.)
(c) The condition of the surface to be macroetched.

Factors connected with the etching reagent itself depend on the nature and concentration.

Factors representing the condition of the action of the reagent on the specimen are:

(a) The duration of the action: "etching time"
(b) The temperature at which the action takes place
(c) The quantity of the reagent as related to the size of the test piece
(d) Conditions of action not mentioned above, such as stirring of the reagent, rotation of the specimen in it, etc.

Evidently in order to establish a more correct method of judging steel by the macroetching effect produced on them by a certain reagent, it is essential to determine the influence and relative importance of each of the above factors. An effort to achieve this aim in a simple experimental way with regard to a reagent which seemed to be most suitable for the conditions of every-day practice was made in the investigation described in the following pages.

Steels Selected for the Experiments

The steels selected covered by their composition the range of forgings and centrifugal castings usual for ordnance work. The test slabs and disks were cut from actually manufactured pieces, and then sectionalized so as to be conveniently used for comparative etching experiments. The preceding treatment of the pieces had to be taken into consideration, as it is well established that other conditions being equal, steels taken as cast respond to macroetching more easily than steels in a forged condition; cold working and annealing facilitate macroetching, and the finishing temperature of forging and the subsequent mode of cooling show their effect as well. This is sufficient to make one realize that unless it is specifically desirable to apply macroetching methods to steels in the very condition in which they are submitted, it is essential for correct comparative judgment to bring them preliminarily to the same normalized state. In Table I are shown the chemical composition, condition with reference to treatment, etc., of the specimens used in the experiment. Carbon, nickel, and molybdenum steels covering the usual ordnance and commercial compositions were also tested during this work, and in connection with the work of the American Society for Steel Treating sub-committee on macroetching, which included all steels of the Society of Automotive Engineers' specifications, and also tool steels and stainless steels and irons.

The data obtained on the above steels as test-pieces were systematically applied in the current macroetching work of the Watertown Arsenal to various steels, and the results were thus checked repeatedly as far as practical use is concerned. The photomacrographs shown later prove the usefulness of the macroetching method developed in this way.

Reagent

In order to select the most serviceable etching reagent it is necessary to consider the practical conditions of its application, and they dictate the following requirements:

1. The reagent must give good all round results, and be applicable to the majority of cases under the usual conditions of industrial work, revealing the greatest possible variety of structural characteristics and irregularities.

Table I
Chemical Composition of Steels Selected for Experiments

Steel No.	Composition C	Mn	Si	S	P	Mo	V	Ni	Cr	Remarks	Brinell Hardness Outside	Bore
1	0.42	0.50	0.25	0.029	0.025	....	....	....	....	As Cast. Not heat treated.	140	159
2	0.42	0.50	0.25	0.029	0.025	....	....	....	....	The same as No. 1 but after heat treatment.	156	207
3	0.43	0.79	0.30	0.037	0.021	....	....	....	0.10	Seamless tube heat treated.	229	207
4	0.40	1.98	0.39	0.024	0.030	....	....	....	....	As Cast. Not heat treated.	207	255
5	0.29	1.19	0.27	0.026	0.032	0.30	....	....	....	Forging. Heat treated.	197	207
6	0.30	0.54	0.139	0.021	0.014	0.41	0.155	....	....	Forging. Heat treated.	197	187
7	0.41	0.56	0.186	0.022	0.010	....	....	3.05	....	Forging. Heat treated.	217	217
8	0.38	0.71	0.24	0.031	0.038	....	....	3.08	....	Forging. Heat treated.	207	207

2. The reagent must be simple in its composition, easily prepared, and inexpensive for mass production work.

3. The reagent must not change its composition on standing, if kept in readiness in stock, and must be as stable as possible under the conditions of using.

4. The application of the reagent and all the operations connected with its use must be simple and easy to perform by a person without much previous experience.

5. The reagent and conditions of its use must not be injurious or unpleasant for persons executing the work.

In view of the great number and variety of reagents offered for macroetching purposes, it was decided to examine and compare them, bearing in mind the above points. Such a review brought forward reagents made up of such ordinary substances as hydrochloric and sulphuric acids. There are several very old recipes for etching solutions comprising both of these acids and water in different proportions, and several recipes prescribing the use of definite concentrations of one acid. It appeared to be practical to try out such solutions first,

and in case of the possibility of better results, to work out a new composition.

Experiments with sulphuric acid alone gave unsatisfactory results, and there were left for consideration water solutions of hydrochloric acid, and mixed solutions of this acid and sulphuric acid.

Numerous recommended compositions of such solutions can be found in use and in the literature. Ordinarily such compositions are expressed in the number of volume units of the liquids to be mixed, from which it is impossible to judge the relative effect of each of the acids used. Though, in general, the action of these mixtures on alloys of such a very complicated structure and nature as present day steels is extremely difficult to bring down to a few chemical formulas, nevertheless some generalization appeared very desirable. In order to facilitate this, it was thought better to abandon the old way of expressing the proportions of the reagents in figures not related to the usual practice in the expression of concentrations. The proportions were recalculated as concentrations per 100 parts of solution by volume, sulphuric acid being taken of "reagent grade" (Sp. Gr. 1.84, 66° Be, 94% H_2SO_4), the same being done with hydrochloric acid (Sp. Gr. 1.19, 23° Be, 36-37% HCl). After rounding the figures, it appeared that the following proportions might serve well as representative macroetching solutions of this type:

A—Hydrochloric acid 70 parts—Sulphuric acid 23 parts—Water 7 parts.
B—Hydrochloric acid 50 parts—Sulphuric acid 0 parts—Water 50 parts.
C—Hydrochloric acid 38 parts—Sulphuric acid 12 parts—Water 50 parts.
D—Hydrochloric acid 10 parts—Sulphuric acid 30 parts—Water 60 parts.
E—Hydrochloric acid 25 parts—Sulphuric acid 10 parts—Water 65 parts.

The first solution, A, is in fact a mixture of the type of Waring's solution, formerly used at Watertown Arsenal with great success. The objections to its use lie in the extremely unpleasant and dangerous handling of such a strong solution, particularly as the etching has to be carried out at boiling temperature. The undesirability of such a reagent for regular work, and when much etching work is to be done, is evident.

The second solution, B, is the reagent at present tentatively recommended by the committee of macroetching of the American Society for Steel Treating (see "Tentative recommended practice for a standard macro etch test for iron and steel"). This is also a reagent of long standing repute, simple in its application, rational in composition, and without any particularly objectionable feature of

handling. For regular work, especially work connected with production, it presents a very convenient tool. The absence of sulphuric acid in the composition partly detracts certain very good characteristics from the results, of which the principal ones are a particular clearness of pattern, a nice fresh coloration of the metal, and considerable stability of the well-washed and dried macroetched surface against rust. The results obtained by the next solution, C, compare favorably with those given by solution B in all these particulars.

The third solution, C, was developed during the investigation. It belongs to the type of comparatively weak acid solutions, and retains the delicate part of the action of both hydrochloric and sulphuric acids. The necessary temperature conditions are easily maintained, and the concentration of the solution is not subject to change during the test beyond the effect of errors and inexactitudes of the macroetching method as a whole.

The fourth solution, D, is remarkable for the predominance of sulphuric acid in its composition. It also belongs to an old type of reagent, and it is mentioned in the standard of the American Society for Testing Materials. The action of the reagent is very much like the action of sulphuric acid alone in corresponding concentrations, and leaves very much to be desired. In order to see whether a decrease of the concentration of the acids together with a reverse change in their proportion would bring better results, solution E was tried. Sometimes reagents of this type are recommended, but apparently without sufficient preliminary systematic comparative study. This investigation has shown considerable disadvantages in their use.

One of the advantages of using solutions of hydrochloric acid containing about 20 per cent HCl by weight lies in the fact that on boiling or heating nearly to the boiling point such solutions do not change materially their concentration with regard to HCl as a 20.2 per cent HCl solution has a constant boiling point (110 degrees Cent. at 760 mm.) and distills as such.

The introduction of sulphuric acid in solution C with a volume ratio of 38-12-50 hydrochloric acid–sulphuric acid–water, does not bring much change in this respect. Direct experiments have proved that boiling 500 cubic centimeters of such a solution for 30 minutes in a 1000 cubic centimeter beaker increases its acidity far less than 3.5 per cent; this means that under usual macroetching conditions only a slight change in the action of this acid reagent may be expected, which may be neglected for practical macroetching.

The usual loss through vaporization of that reagent during an ordinary macroetching operation is about 10 per cent by volume; naturally this loss depends on the area of vaporization, i.e., on the shape of the dish in which the etching is performed.

The experiments were carried out with hydrochloric and sulphuric acids of "reagent grade" which has a low content of impurities. As there is no necessity to use this comparatively expensive grade of acids in regular routine macroetching work, ordinary acids, existing in the chemical trade under the name of "technical grade" acids, could be used with the same success, provided that the acids are supplied by a reputable chemical trading firm, which may serve as a guarantee that the acids comply with the usual standards regarding impurities.

In the trade there are three principal "technical grades" of hydrochloric acid:

18° Baumé, sp. gr. about 1.14, containing approx. 28% HCl by weight.
20° Baumé, sp. gr. about 1.16, containing approx. 33% HCl by weight.
22° Baumé, sp. gr. about 1.18, containing approx. 35% HCl by weight.

Chemically pure, "reagent grade" hydrochloric acid has usually the following characteristics:

23° Baumé, sp. gr. about 1.19, containing approx. 36-37% HCl by weight.

If the composition of the etching reagent is expressed by volume ratio: 38-12-50 of hydrochloric acid, sulphuric acid, and water for the "reagent grade" acids, the corresponding composition in the case of the above mentioned technical grades of hydrochloric acid will evidently be:

49 - 12 - 30 for the acid of 18° Baumé
42 - 12 - 46 for the acid of 20° Baumé
39 - 12 - 49 for the acid of 22° Baumé

As for the quantity of sulphuric acid, if the ordinary "technical grade 66 acid" is used, there is no need to introduce any correction as this so-called "technical 66 acid" has a specific gravity of 1.83, or 66° Baumé, and contains about 93.2 per cent of H_2SO_4, while the characteristics of the "reagent grade" acid are: Sp. gr. 1.84 or 65.9° Baumé and 94 per cent content of H_2SO_4, the difference being quite negligible for the purpose.

In order to simplify the practice, the following proportions by volume were tried as a substitute for reagent C:

Hydrochloric acid,	sp. gr. 1.14	- 50 parts
Sulphuric acid,	sp. gr. 1.83	- 10 parts
Water,		- 40 parts

or

Hydrochloric acid,	sp. gr. 1.18	- 40 parts
Sulphuric acid,	sp. gr. 1.83	- 10 parts
Water,		- 50 parts

The results of etching with a reagent of such compositions did not, for all practical purposes, differ much from those obtained by using the more exact proportions.

In general it is a simple chemical problem to calculate the proper proportions of water and the acids if the latter are available only in some odd concentrations. The best method of preparing the reagent mixtures is to measure the three liquids (water and the acids) separately in separate dishes in the usual way, and then mix them together, first adding the sulphuric acid to the water very gradually in order to avoid heating of the solution, and then, when the solution is cool, carefully adding to it the measured quantity of hydrochloric acid.

Reagents A, B, C, D, and E prepared as described above, were subjected further to a series of comparative tests in order to determine their relation to various factors affecting the success of the macroetching test, and to ascertain their relative suitability as a "standard reagent" when used under every day production conditions.

One of the first comparative tests was to determine for these reagents their relative macroetching effectiveness, in other words the extent of relative chemical action, which may be measured by the amount of substance of a selected metal specimen "eaten out" or "dissolved" under certain definite conditions of the experiment. After all, it is the chemical action taking place between the reagent and the test piece (on its surface), which constitutes the ultimate cause of the appearance of the macroetching pattern. It is quite natural to measure the amount by the loss in weight of the specimen calculated for a unit of its surface (1 sq. in. or 1 sq. cm.). Such a determination of loss in weight was made for specimens of each of the eight steels shown in Table I in each of solutions A, B, C, D, and E. All the specimens were macroetched under the same conditions of time (30 min.), temperature 200 degrees Fahr. (95 degrees Cent.), rela-

Table II

Comparison of Etching Effect of Reagents A, B, C, D and E

Steel	A 70-23-7 (W.A.)	B 50-0-50 (S.S.T.)	C 38-12-50 (New W.A.)	D 10-30-60 (S.T.M.)	E 25-10-65
1	Maximum loss in weight as compared with the other solutions. Satisfactory but not so rich in details as 1C.	Over-etched. No satisfactory details.	Good, contrast etch, very fine details and variety of them. Very suitable for photographing.	Etch may be regarded as satisfactory, but surface dark, without such a good contrast as 1C.	Minimum loss of weight. Bright, but not contrast enough. Apparently different constituents are equally rapidly eaten out.
2	Maximum loss in weight as compared with the other solutions. Satisfactory but not so rich in details as 2C.	Over-etched, details disappeared.	Good contrast etch, with fine details and variety of them. Very suitable for photographing.	Fine details, but no contrast.	Minimum loss of weight. Etch much like C.
3	Maximum loss in weight as compared with the other solutions. Over-etched; details disappeared.	More over-etched than 3A.	Over-etched, but not so bad as 3B or 3D.	Minimum loss of weight. Over-etched, but not so much as 3A or 3C.	Over-etched, as badly as C. Details are eaten away.
4	Maximum loss in weight as compared with the other solutions. Good etch. Nice clean surface.	Over-etched, too much contrast.	Good etch, delicate details preserved, segregations shown well. Good for photographing.	Good etch, with some contrast, but darker color than 4C.	Minimum loss of weight. A little over-etched, not so distinct as C.
5	Maximum loss in weight as compared with the other solutions. Over-etched.	Details developed satisfactorily.	Minimum loss of weight. Details developed satisfactorily.	Not clean appearance, darker colors all over.	Not clean appearance, details not worked out.
6	Maximum loss in weight as compared with the other solutions. Not distinct etch.	Details developed satisfactorily.	Details developed satisfactorily.	Not clear appearance, darker color all over.	Minimum loss of weight.
7	Maximum loss in weight as compared with the other solutions. Even etching; but not enough contrast in affecting dendrites and other components.	Over-etched, fine details disappeared.	Minimum loss of weight. Not sufficient etching, without enough contrast.	Less sufficient etching than 7C, no details.	Not sufficient action, very much like 7C and 7D.
8	Maximum loss in weight as compared with the other solutions. Over-etched.	Over-etched.	Good even etching, very suitable for photographing. Fine details of dendritic structure well preserved. Nice, clean, bright surface all over.	Minimum loss of weight, good etching, though not so full of details as 8C.	Over-etched.

tive quantity of the reagent, and preparation of the surface, which suited the average practice in carrying out usual tests. The total surface of each of the specimens was measured, their weights before and after macroetching were determined, and the loss per unit of surface was calculated. All the data obtained in this way, together with the observations regarding the macroetching effect produced, are tabulated in Table II. The losses per square inch of surface are presented graphically in Fig. 1.

It is evident from these results that the loss of weight per square inch of all the steels is considerably smaller in reagent C than in

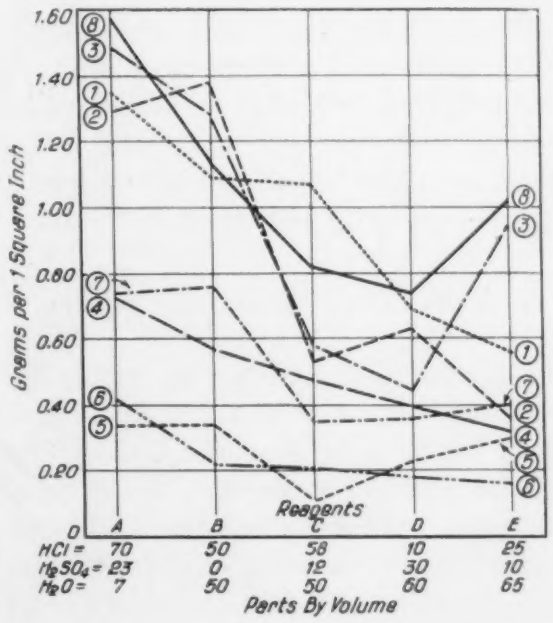


Fig. 1—Graph Showing Loss of Weight in Grams per Square Inch for Various Steels (see Table I) in Etching Solutions A, B, C, D, and E.

reagent A, it is markedly smaller in C than in B, and for steels 8, 3, 7, and 5 still smaller; but for steels 1, 2, 4, and 6 larger in C than in E; in the case of reagent D, the loss for all steels excepting 2 and 5, is below that of reagent C (see Fig. 1). Apparently, all other conditions being equal, for the rather weak concentrations selected, an increase in the relative concentration of sulphuric acid diminishes the loss in weight of the metal. It was thought that this fact is of importance from the point of view of overetching, and also psychologically, in avoiding the usual objections of too drastic treatment in macroetching methods. This fact was also made use of in working

out the proportions of the acids for the new solution C. The action of reagent A, remarkable for its very strong etching effect, is different from a chemical point of view, as it is mostly due to the effect of concentrated acids under high temperature. It is evident that of two macroetching reagents, giving equally good pictures with the same fullness of detail, the one having a less corrosive and more delicate action is preferable. Solution C presented great interest in this respect, and experiments described later confirmed its superiority over other tested solutions. For the majority of steels it produced the most delicate details in pattern, gave a better, brighter, and cleaner surface, more stable with regard to tarnishing (oxidation), provided the specimens were well washed and dried after macroetching. That solution is easy, not unpleasant, and not dangerous to handle, is sufficiently little sensitive in its effect to variations in temperature and etching time, and is stable enough in its relative concentration of separate ingredients on being heated and in storage. All these facts are of great importance in practical work.

Preparation of Specimens: Their Size, Shape, and Surface

The size, shape, and finish of the surface of the specimen selected for macroetching are of importance. Large heavy pieces are difficult and troublesome to handle in acid solutions, pieces that are too long and narrow require containers of an unusual shape, and an unnecessary excess of reagent. Usually thin disks and slabs are the most convenient for handling, if their dimensions do not much exceed 10x10x¼ inches. It must be remembered that often one extra saw cut, judiciously made, leads to better results in etching, and to considerable economy in time and materials.

In general, selection of the method and directions for sectionalizing of a piece of metal to be subjected to metallographic investigation must be made with proper consideration of the aim of the test. Often this condition is disregarded, and the results of the tests, if not quite lost, do not yield fully all possible information.

With regard to the surface on which the macroetching pattern has to be revealed, it is essential to have it of such good finish that after sufficient action of the reagent, it would not show any traces of tool marks, which interfere with the regularities of the picture produced by etching. Such marks can seriously mask some delicate but important details, and make the proper interpretation of the results

impossible. On the other hand, in order to make the etching most useful for production work, preparation of the surface has to take the possible minimum of time and labor. While for very drastic and very deep etching a surface with a very coarse finish can be satisfactory, for delicate etching, where fine details are desirable and small variations in the time of etching are considered important, the finish of the surface must be accordingly fine enough.

Special experiments made in this investigation proved definitely that for macroetching with the reagents described above, polished surfaces are not necessary; at the same time, the surface produced by cutting with a hack-saw, even a very fine one, is not desirable, as the cut marks often appear on the etched surface, distorting the pattern. Though in such cases a very experienced observer may avoid errors in judgment of the metal, it is in the interests of proper inspection to use a better surface finish. This could be accomplished by filing the cut surface with a fine file, and by finishing it with emery paper No. 0 or No. 00. Very constant and extremely satisfactory results, however, have been achieved by using surfaces prepared by grinding on surface grinders with Norton grinding wheels of "38 Alundum" or "19 Alundum" brand of soft or medium grades, and of 80 or 90 grain size. For instance, a wheel of usual Norton designation "3880-J," always gave excellent results. It is of importance to insist on small feeds (within 1/500″-1/1000″) during the grinding operation in order to avoid "burning" of the metal, the effect of which, if deep enough, shows itself after etching by an appearance of a series of dark parallel stripes on the surface, due to a local structural transformation in the metal. The danger of burning is easily avoided without any loss of time by a little more attention to the work.

In order to speed up the work of grinding larger pieces (up to 16″ in diameter), a grinding machine with grinding disks having horizontal axes was tried and used at the Watertown Arsenal. It was a usual No. 6—26″ Gardner disk grinder, manufactured by the Gardner Machine Co., Beloit, Wis., with a corrugated disk of 26″ diameter, and a speed of rotation of about 1200 revolutions per minute. An exact specification of the disk is the following: No. 167, grade 2x deep corrugated 26x6x⅜ G. I. A. disk. The corrugations play an important part in effecting the cooling of the surface of the metal, and preventing "surface burning," which may be the cause of serious errors in the interpretation of macroetchings and Baumann prints. The piece of metal to be ground is gripped in a special holder

mounted opposite the disk, and is pressed by a lever to its surface. The lever is designed so that the location of the face of the piece can be constantly changed relative to the position of the center of the grinding disk by simple movements of the lever. The results obtained were satisfactory in general, though altogether the machine is somewhat clumsy, and requires too much attention on the part of the operator. The time usually required for grinding one disk of 8 to 10 inch in diameter varies between one half and one hour, depending on the roughness of the surface obtained by the rough saw. For better work, and for pieces of smaller size, the surface grinders of Brown and Sharpe type are, no doubt, preferable.

Altogether, from a practical point of view, preparation of the surface for macroetching by surface grinding, as indicated above, appears to be by far the most suitable method, which is easily carried out in any workshop or even in an up-to-date metallurgical laboratory, since small surface grinders are a very useful and even necessary part of laboratory equipment, where they prevent loss of time, and add to the perfection of metallographic work.

The characteristic appearance of the ground surface of unetched specimens regarded as having a satisfactory finish for the macroetching operation is shown in Fig. 2; the direction of the light was purposely so arranged as to make the tool marks well noticeable.

The surface of a specimen to be macroetched has also to be considered in connection with the quantity of the reagent required for a test. It really determines the amount of reagent necessary for the macroetching action itself, the total mass of the specimen having no direct bearing in this respect, though the shape is of importance. In general it is simple to calculate on the amount of acid reagent required for the macroetching action proper, but a certain excess of reagent is necessary to produce the effect. This excess can be determined only by experiment, and such experimental data are offered for reagent C (HCl conc.: H_2SO_4 conc.: H_2O = 38:12:50 parts by volume) in Table III. This Table may help avoid reagent waste, but is not always applicable. The shape of the dish in which the etching is done, or the shape of the piece may sometimes be such that a larger quantity of the reagent than given in the table may be required to cover the piece completely with the liquid. In such cases an additional quantity of the reagent is necessary because all of the piece must be well under the surface in order to prevent uneven etching.

The use of a partly spent etching reagent over again is to be

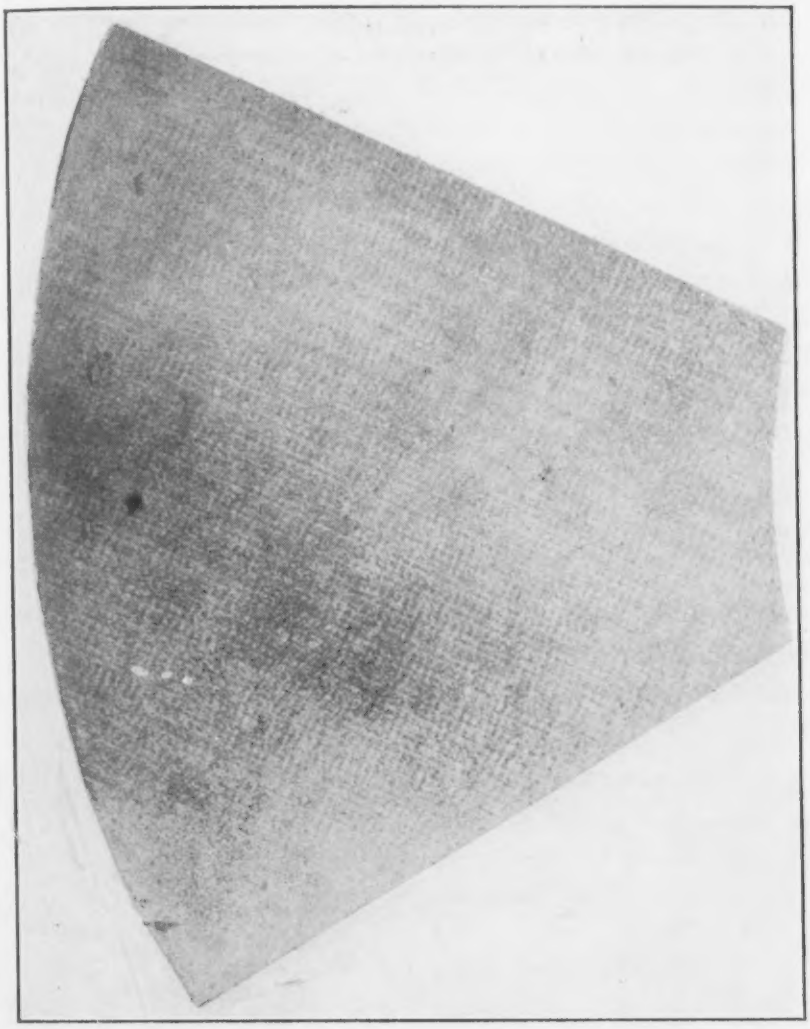


Fig. 2—Typical Appearance of a Surface Properly Prepared for Macroetching by Grinding. The Light is Directed so as to Show Tool Marks. Carbon Steel, Partly Tarnished.

avoided if certain and good results are desired. The low cost of the technical grade acids makes any possible economy in this respect insignificant.

Etching Time

The etching time or duration of action of the acid reagent on the specimen is one of the most important factors in macroetching. In general, all other conditions being equal, the longer the etching time, the stronger the effect of macroetching; if the etching time is insufficient, the picture obtained on the specimen may be incomplete, the structure of the piece with many important details not sufficiently

Table III
Practical Table for Determination of Quantity of Reagent, Required for Macroetching

Surface of the specimen in sq. inch.	1	2	3	4	5	6	7	8	9	10	15	20
Volume of Reagent in cubic cent.	75	125	150	185	225	250	270	295	310	340	440	540
Surface of the specimen in sq. inch.	25	30	35	40	45	50	55	60	65	70	75	80
Volume of Reagent in cubic cent.	610	680	750	820	880	950	1000	1090	1150	1200	1250	1300
Surface of the specimen in sq. inch.	85	90	95	100	110	120	130	140	150	160		
Volume of Reagent in cubic cent.	1350	1400	1450	1500	1600	1650	1750	1850	1900	2000		

outlined, and conclusions regarding the quality of the metal will be incorrect. On the other hand, if the etching time is too long, the appearance of the metal to an inexperienced observer may suggest a

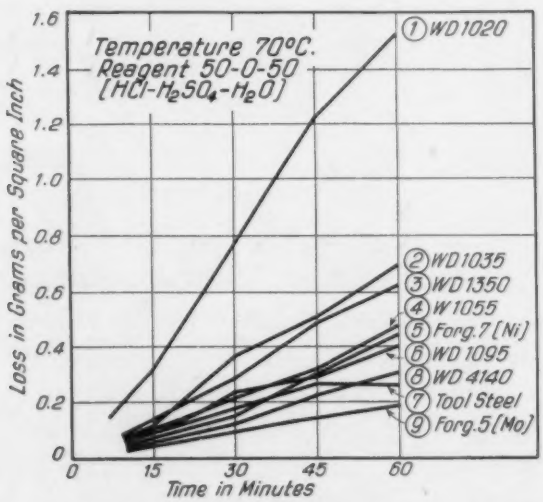


Fig. 3—Graph Showing the Influence of Time on Loss of Weight for Different Steels.

metal much worse than it is in reality. As the action of the etching reagent consists in the first place in "eating out" or dissolving in the acids those constituents which are more easily attacked by the reagent, their location will be marked by hollow spaces, cavities, and holes; in the beginning of the etching process such places usually

show themselves as fine spots, but with time their dimensions grow far beyond the real size of these components, which are present as nonmetallic inclusions, sulphides, phosphides, etc., and which constitute the undesirable parts of the metal. Sometimes it is possible that after a too prolonged etching, the macroetched surface shows a better metal than does a short etching. This is because the first sharp outlines of easily attacked regions, which always gives an unpleasant impression of abrupt discontinuity, lose their definite appearance with time; the metal, yielding to the action of the acids less quickly, is attacked, the sharp edges of its dendrites become rounded off, and the general appearance of the surface becomes smoother and less ugly looking than in the first stages of macroetching. For this reason it is very desirable to note the changes on the surface of the pieces at the beginning of the etching, and bear them in mind when making the final decision about the metal. The composition of the steel greatly influences the time necessary to produce the macroetching effect. Experiments were made to collect definite data on this point, and the results shown in Fig. 3 and Table IV where the

Table IV

Effect of Time on Loss in Weight of Different Steels When Etched in 50-0-50 (HCl-H_2SO_4-H_2O) Reagent at 70 Decrees Cent.

		Loss in grams per square inch after etching for				CHEMICAL COMPOSITION						
Curve	Steel	15 Min.	30 Min.	45 Min.	60 Min.	C	Mn	Max. S	Max. P	Ni	Cr	Mo
(1)	WD 1020	0.32	0.78	1.23	1.53	0.15–0.25	0.30–0.60	0.05	0.045	....	.....	.....
(2)	WD 1035	0.12	0.37	0.51	0.70	0.30–0.40	0.50–0.80	0.05	0.045	....	.....	.....
(3)	WD 1350	0.14	0.29	0.49	0.63	0.45–0.55	0.90–1.20	0.05	0.040	....	.....	.....
(4)	WD 1055	0.11	0.22	0.32	0.48	0.50–0.60	0.40–0.70	0.05	0.045	....	.....	.....
(5)	Forging 7	0.08	0.16	....	0.45	0.41	0.56	0.022	0.010	3.05	.....	.....
(6)	WD 1095	0.10	0.23	0.30	0.41	0.90–1.05	0.25–0.50	0.05	0.040	....	.....	.....
(7)	115	0.10	0.18	0.27	0.26	1.15	0.15–0.35	0.05	0.040	....	.....	.....
(8)	WD 4140	0.06	0.13	0.23	0.31	0.35–0.45	0.40–0.70	0.045	0.040	....	0.80–1.10	0.15–0.25
(9)	Forging 5	0.05	0.10	....	0.19	0.29	1.19	0.026	0.032	....	.....	0.30

correlation between loss in grams per square inch and etching time in minutes for nine different kinds of steel are shown. The experiments refer to reagent B, representing a solution of 50 volumes of hydrochloric acid and 50 volumes of water, used at 158 degrees Fahr. (70 degrees Cent.) in a regular way for etching specimens of each of the above nine steels for 15, 30, 45 and 60 minutes. The pieces were weighed before and after macroetching, and the corresponding losses in weight were determined. The diagram in Fig. 3 shows

well how rapidly the loss in weight grows with time for plain carbon steels of 0.20 per cent and lower carbon content, and how rapidly this loss decreases with an increase in the carbon, and how comparatively slowly it varies for nickel and molybdenum steels. These curves show plainly that if we consider the loss of about 0.3 grams per square inch as normal for producing a good macroetching effect, we have to choose 15 minutes as the etching time for carbon steels of 0.20 per cent and lower carbon content; 25-30 minutes for steels of 0.30-0.50 per cent carbon, and about 45 minutes for carbon steels of 0.55-0.95 per cent carbon content. It is interesting to note how these figures for etching time coincide with the figures recommended by the macroetching committee of the A. S. S. T., and selected purely by comparing the appearance of pieces etched for various periods of time. It is evident that it is impossible for a given reagent to establish one standard etching time for all kinds of steels; such a time has to be determined experimentally for steels of different composition by separate etching tests; even then, always taking into consideration possible variations in heat treatment and other conditions, this etching time can be regarded only as approximate data, departures from which are necessary, depending on each given case, and on the experience of the person conducting the macroetching.

It is also evident that reagents not so vigorous in their action, in other words, reagents giving "loss per square inch-time" curves (like the curve in Fig. 3) of lesser slope, allow more latitude with regard to time and make it easier to attain proper results in etching. It is remarkable that reagent C (38-12-50) showed itself similar in this respect, and even perhaps more favorably, to reagent B (50-0-50), as can be judged from the diagrams in Figs. 1, 3, and 4. The fact was foreseen after the first preliminary experiments, and this circumstance was one of the factors in the development of the composition of reagent C.

In general, the etching time as determined for different steels by the committee on macroetching of the A. S. S. T. for etching reagent B (50-0-50), can be applied when using reagent C; but with regard to both reagents it is important to remember that this time is an approximate minimum for normalized steels, and that always there may be a case when it is necessary to prolong the etching in order to better develop certain special details. An instructive example of the effect of prolonged etching is shown in Fig. 5. Usually it has to be remembered that a longer time is necessary if a cold specimen is put into the

reagent without preheating. If the specimens are large, a considerable allowance in time has to be made on this account. Ordinarily a little experience is sufficient to get good practical results in such cases. For convenience of the reader the table of "etching times," as established by the Recommended Practice Committee of the A.S.S.T. and published in the 1930 edition of National Metals Handbook is given below.

Recommended Etching Time for Various Steels

S.A.E. Carbon Steels	
Steels	Minutes
1010	15
1015	15
1020	15
1025	30
1030	30
1035	30
1040	30
1045	45
1050	45
1095	45
1315	30
1350	30
1360	30

S.A.E. Nickel Steels	
2315	30
2320	30
2330	30
2335	30
2340	30
2345	30
2350	30
2512	30

S.A.E. Nickel-Chromium Steels	
Steels	Minutes
3115	45
3120	45
3125	45
3130	45
3135	45
3140	45
3215	45
3220	45
3230	45
3240	45
3245	45
3250	45
3312	60
3325	60
3335	60
3340	60
3415	45
3435	45
3450	45

S.A.E. Chromium Steels	
5120	30
5140	30
5150	30
52100	45

Tool Steels	
	Minutes
Carbon and Carbon-Vanadium	45
Manganese Oil Hardening	30
Fast Finishing	45
Tungsten Hot Die Steel	45
Chromium Hot-working Die	45
High-Carbon-High-Chromium	45
High Speed	45

S.A.E. Chromium-Vanadium Steels	
Steels	Minutes
6120	45
6125	45
6130	45
6135	45
6140	45
6145	45
6150	45
6195	45

S.A.E. Molybdenum Steels	
4130	45
4140	45
4150	45
4615	45

S.A.E. Silico-Manganese Steels	
9250	30
9260	30

Stainless Steels	
Stainless Irons	30
Stainless Steels and 18-8 Stainless Steels	45

S.A.E. Tungsten Steels	
Steel	Minutes
71360	45
71660	45
7260	45

Temperature of Macroetching

The temperature at which etching takes place affects the speed of action of acids, i.e., the loss of weight per square inch of surface of the metal, or the depth to which macroetching penetrates the surface of the specimen at a given time. Naturally for steels of different composition, condition, and heat treatment, the influence of the temperature will vary. As there were no sufficient data in the literature giving any quantitative correlation in this respect, it was de-

cided to determine experimentally the approximate character curves representing the changes in loss of weight per square inch with changes in temperature for several typical steels and such typical reagents as B (50-0-50) and C (38-12-50). These curves are shown in Fig. 4. The loss was determined by etching the specimens for 30 minutes (the usual average etching time) at different temperatures, and weighing them before and after the experiments.

A study of the curves reveals great similarity in the action of both reagents B and C with regard to etching time, and shows that reagent C is no more drastic than B. Apparently the temperatures selected as standard for solution B ought to bring the same results in the case of solution C, if the duration of macroetching will be somewhere about the usual etching time for steel—30 minutes, with some

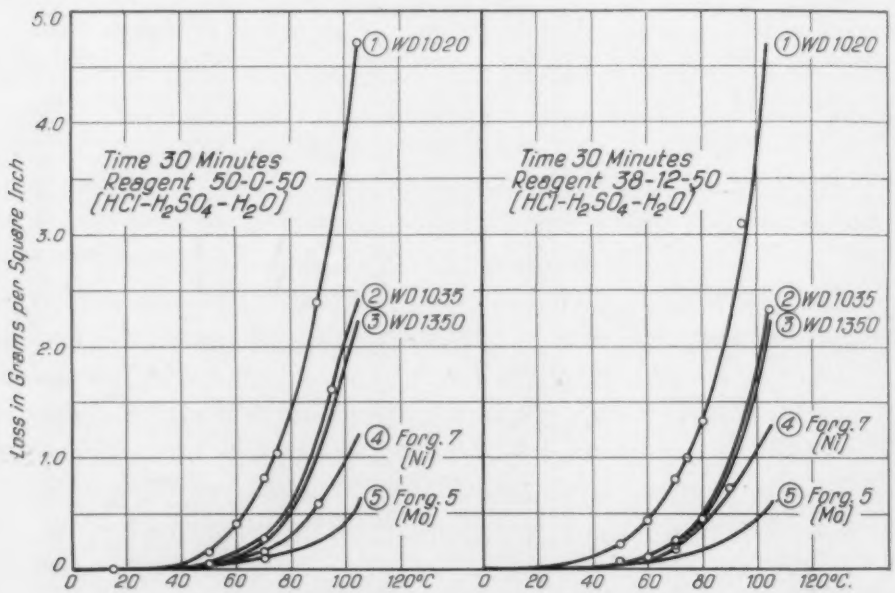


Fig. 4—Graph Showing Influence of Temperature of Etching on Loss of Weight of Different Steels for Reagents B and C.

variations in both directions. Thus, substituting reagent C for reagent B will involve no change in the macroetching action as far as the temperature is concerned. But if for both reagents a temperature of about 212 degrees Fahr. (100 degrees Cent.) instead of 71 degrees Cent. (160 degrees Fahr.) (as accepted by the committee of the A. S. S. T. in the "Tentative recommended practice for a Standard Macroetch Test"), the loss of weight during the same period of etching will increase for steel WD1020 about four times; for steels WD1035 and WD1350 about 6-7 times; for Ni-steels about 3-4

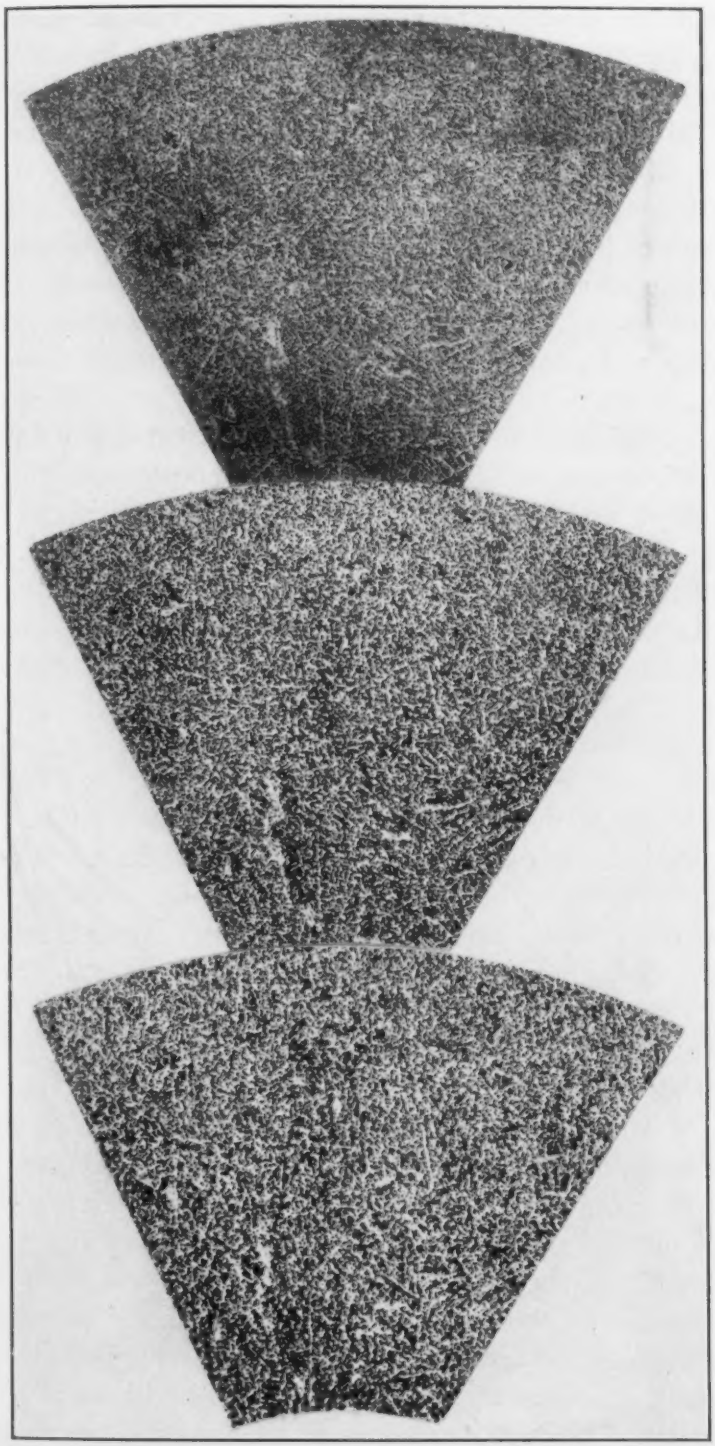


Fig. 5—Effect of Etching Time: Changes Produced on the Same Area of a Piece of Steel (No. 8 in Table I) by Taking the Time 10, 35 and 80 Minutes Respectively.

times; and for Mo-steels about 3-4 times; as can be seen from the curves in Fig. 4. However, further experiments have proved that while the curves showed well that the etching action of both reagents B and C changes in a very similar manner with the temperature it would be advisable from more practical considerations to test the "etching times" determined for reagent B on reagent C, but at the temperature of boiling instead of 160 degrees Fahr. this would give the advantage of avoiding the necessity of measuring and keeping the temperature of the hot acid mixtures at 160 degrees Fahr., which is a troublesome and unpleasant operation under the conditions of practical work.

The experiments described previously, when discussing the nature and concentration of the reagents, and represented by the diagram in Fig. 1, and by Table II, definitely proved the milder action of reagent C. This, taken together with the character of the curves in Fig. 4, suggests that the etching times for this reagent at a temperature of 160 degrees Fahr. will be shorter than those for reagent B, and also makes it reasonable to expect that the "boiling point etching times" for C may not differ very much from the 160 degrees Fahr. etching times for B. Actual experiments with various steels confirmed this, and proved that when using reagent C at a temperature near its boiling point, the same etching times could be taken as those recommended for B at 160 degrees Fahr. (71 degrees Cent.), because reagent C has considerable latitude in its etching action with regard to the etching time, which makes certain variations in the time quite admissible without affecting appreciably the picture produced by macroetching. The last fact appeared to be of particular practical value, especially in view of the impossibility of strictly standardizing all conditions of the macroetching test, and of the necessity of allowing wide margins for errors in the estimation of the initial temperatures of the test pieces and of the reagent, in keeping the etching time, and in the estimation of the defects in the metal as affected by the extent of the macroetching action. The experience and knowledge of the persons carrying out the test, brings here a factor covering to a great extent such impractical and superfluous demands as keeping the temperature of the macroetching bath at 160 degrees Fahr. (71 degrees Cent.). It has to be borne in mind that considerations of practical conditions in the technical laboratories and in the workshops (where the tests have to be carried out sometimes) make it desirable to avoid troublesome and exact measurements of

temperatures, and to select as a standard the boiling temperature of the reagent, and to keep the reagent just at the simmering point in order to prevent excessive evaporation. In this way, the control of the conditions of the bath will consist only in the observation and regulation of boiling. Reagent C, as evident from the above, has such a composition that when boiling under usual conditions of work, it does not change its action beyond the satisfactory practical limits. Also the action is slow enough to make harmless such variations in the etching time for different steels as invariably occur in practical circumstances.

After the foregoing experiments and general considerations pertaining to the separate, principal factors influencing the macroetching picture, it may be of interest to see what general procedure is to be pursued in carrying out the macroetching test. The following presents the practice established at the present time at the Watertown Arsenal.

General Procedure in Macroetching

The general procedure in macroetching after the surface of the specimen has been properly prepared, cleaned and wiped with gasoline or some suitable solvent to remove any traces of oil (which may cause uneven etching), it is put into a suitable dish (glass, porcelain, stoneware, etc.) covered with clean water and heated in the water to etching temperature. When the piece has acquired the proper temperature, it is taken out, carefully placed into the etching dish like the above, but containing the proper quantity of the etching reagent already heated* to its simmering temperature, and the time is noted. Often, however, the large size of the piece to be macroetched makes impracticable and unpleasant the operation of transferring it for preliminary heating into a separate dish, and also of taking the piece out of hot acid for washing. In such cases, with a little practice, it is quite easy to obtain the same results by placing the piece in the dish, adding to it the reagent already heated, and pouring it off, either directly or by syphoning, after the usual "etching time," somewhat prolonged because of the low temperature of the piece during the first period of etching; the first washing can be done in the dish, and then finished with the cooled piece taken out. It is possible, of course,

*A gas or electrical hot plate may be used for heating the container of the reagent; sometimes Duriron pots, serving as containers, are heated directly by gas; immersion electric heaters, protected by acid-proof covers present a very attractive method of heating in this case.

to heat the piece preliminarily in water, to pour the water off and then to add the heated reagent. Such a procedure diminishes the correction for etching time, but it is scarcely necessary, as for usual conditions the difference in time from the previous method is not considerable. In the case of using a cold reagent on cold specimens the "etching time" must be increased considerably, usually for the period necessary for heating the reagent to the temperature of etching. The size of the piece, because of great heat conductivity and small specific heat of the metal, is not of such importance in this respect as the quantity of the reagent used, and this has to be considered in determining the time of etching. Usually in such cases the time established for etching of preheated specimens in preheated reagents may indicate the minimum period, after which the piece has to be examined in order to establish by the appearance of the piece the length of further etching. Again, experience and practice give here the best indications, which is of great importance, as this method of work: starting etching with a cold specimen and in a cold reagent, is often the only practicable one in working conditions. At the Watertown Arsenal it is used principally.

After the elapse of selected "etching time," the piece is taken out of the solution, rinsed well under the tap with plently of water and carefully rubbed all over with a soft brush in order to eliminate all dirt and slimy carbon deposit, covering the surface. After repeated rinsing the etched face is carefully wiped with a clean linen or paper towel, and the piece is well dried either in a stream of warm dry air from a special laboratory electric dryer, used often for metallographic work, or just by putting it on a clean hot plate for a few minutes, avoiding unnecessary extreme heating and the effect of the gas or products of its combustion coming from under the plate, which may tarnish the macroetched surface. Sometimes after washing the specimen with water, it is rinsed with alcohol in order to help to eliminate the last trace of water present on the piece in the cavities, in the small pores, and in the cracks which may contain traces of acid, and thus cause tarnishing of the macroetched surface. Sometimes it is also recommended to boil the etched piece for the same purpose in distilled water before drying it. All those measures are excellent, but after some practice and experience it is possible to achieve remarkably good results, just by simple good washing under the tap and careful drying on a hot plate. Such is the regular procedure at the laboratory of the Watertown Arsenal, and experience shows, that

macroetched pieces, finished in this way, preserve their surface in good condition, without tarnishing for many days and weeks.

Cleaning Macroetchings

Very often the contrast of the picture on macroetchings may be improved by carefully rubbing their surfaces with a very fine crocus or emery cloth, but, the writer's experience is, that cleaning the macroetched surface with an ordinary soft rubber eraser, such as is used by a draftsman, greatly improves it and brings out the finest details. Pieces left after macroetching for weeks and even a month or two in the laboratory, after cleaning in this way, looked quite fresh and full of details, and gave excellent photographs.

It is often desirable to preserve macroetchings for long periods, and many substances for covering the surface are recommended for that purpose. However, a freshly etched surface, not covered with anything is best suited for judging the metal, and only delicate cleaning, as with the eraser just mentioned, and the "citrate" method described below, may be regarded as not interfering with the interpretation of details.

Macroetched specimens covered with rust after prolonged exposure to corrosive action can easily be "cleaned," so that the pattern developed by macroetching may be, practically speaking, completely reinstated. Simple treatment: immersion, soaking and rubbing with 5-20 per cent solutions of sodium or ammonium citrate (citric acid itself as well as other salts of it are helpful, too), followed by rubbing with a brush, thorough washing with water and careful drying on a hot plate, does the trick admirably. In general, the duration of the soaking operation may be prolonged for several days, depending simply on the extent to which the macroetched surface has been damaged by rust, but heating to a boiling point usually shortens the operations to an hour or a small part of it. Fig. 6 shows the results obtained by simple soaking.

It is remarkable that the surface of the specimens cleaned by this "citrate" method keeps the bright appearance of the macroetched pattern, resisting corrosion considerably better than could be expected. This fact indicates that in certain cases it is advisable to subject to this "citrate" treatment specimens macroetched in the usual way.

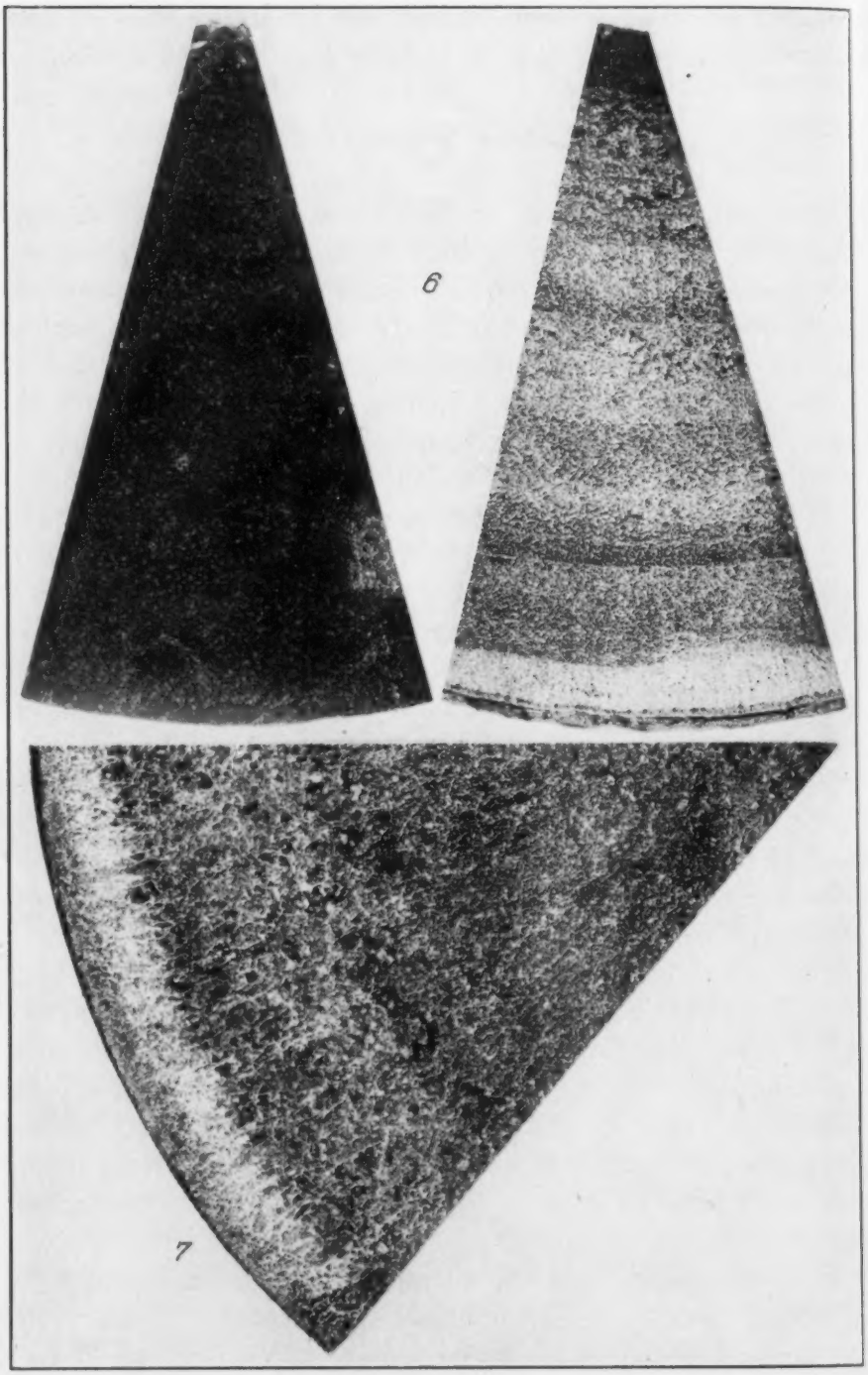


Fig. 6—Results of Cleaning a Rusty Macroetched Piece with a Sodium Citrate Solution. Surface Before and After Cleaning.
Fig. 7—Results of Macroetching by the Citrate Method, which is Being Developed.

A New Macroetching Method to Develop Finer Details

The peculiar chemical action of citric acid and citrates on oxides and compounds of iron suggests their use as etching reagents. Reaumur (1683-1757) in discussing the means of distinguishing bad steel from good, and particularly of determining whether

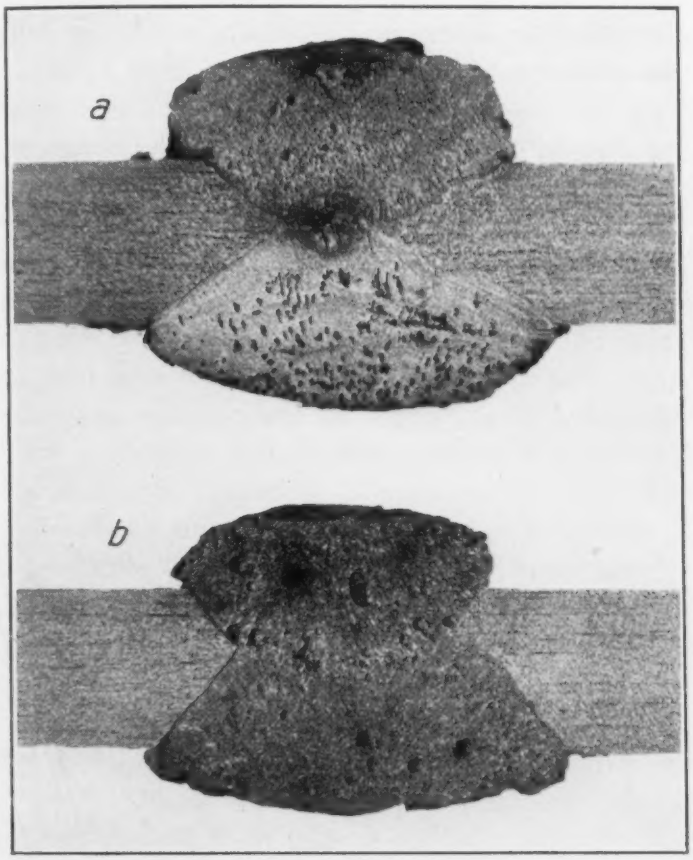


Fig. 8—Examples of Macroetchings of Arc Welds Made on ¼-inch Nickel Steel Plate with Welding Rods of Different Compositions: a.—Cr-Va Steel Rod; b.—Low C-Va Steel Rod.

sword blades and daggers were of real Damascus steel, advised squeezing the juice of a piece of lemon onto the blade and watching the character of the pattern developed. At Watertown Arsenal the author tried to apply and expand these ideas, and found that a very delicate macroetching pattern may be easily developed by using citrates (sodium citrate, etc.), which in many cases is superior and more suggestive for interpretation and understanding of the technological story told by the pattern, than

the etchings obtained by usual ways. While the method is not worked out finally, the Arsenal laboratory uses it successfully. The practical side consists in the preparation of the surface of the specimen in the usual way (though, perhaps, with less attention and accuracy) than in subjecting the surface to the oxidizing (rusting) effect of some medium like water, steam containing bromine, chlorine, iodine, or hydrogen peroxide, or simply exposure for ordinary rusting; immersion in some oxidizing bath is also effective, the principal aim being the creation of a uniform layer of oxides on the surface of the specimen. The following boiling or more or less prolonged immersion of the piece in 5-20 per cent sodium citrate (or other citrate) and good brushing, washing with water and drying complete the procedure. Often the layer of oxides formed during the oxidation period comes off on immersion in the citrate solution as a film, having a pattern on the side facing the surface of the piece, which resembles the macroetched picture produced on that surface. One of the advantages of this method is that the action of the reagent is not drastic, the picture obtained is not exaggerated, and inclusions such as sulphides remain in their places. A Baumann print taken from the surface of the specimen usually gives a full picture of the distribution of the sulphides present. Fig. 7 illustrates the results obtained. The resistance to rusting in the air of the specimens macroetched in this way is quite surprising.

Conclusions

The following are the principal conclusions which may be drawn from the above considerations.

1. It is possible to select several macroetching reagents, simple, convenient and inexpensive in their composition and method of application, which can give very good and comparable results for a very wide, nearly complete, range of steels, used in ordnance work and in usual industrial applications.

2. These reagents belong to a group of acid reagents, and the most suitable of them proved to be of a composition by volume: 38 parts of hydrochloric acid, 12 parts of sulphuric acid and 50 parts of water, hydrochloric and sulphuric acids being both of "C.P." grade, and correspondingly of 1.19 and 1.84 specific gravity or of 36-37 per cent of HCl and 94 per cent of H_2SO_4 content. The usual, so-called, "technical" grades of the acids may

be used with the same success, but the relative composition of the solution by volume has to be changed in accordance with specific gravity of HCl and H_2SO_4 content of the acids. A mixture of 40 parts of hydrochloric acid, 10 parts of sulphuric acid and 50 parts of water (parts measured by volume and acids of "concentrated grade") may be used satisfactorily for usual practical purposes.

3. Though coarsely finished, or even, in some cases, quite unfinished, surfaces of test pieces may be used for macroetching, the judgment of the quality of the metal under such conditions, unless only surface defects are considered, is doubtful and often practically impossible; very fine polished finish of surfaces is superfluous. It was found that surfaces obtained on surface grinding machines, using Norton grinding wheels of 80 or 90 grain size with small feeds (about 1/500-1/1000 of an inch), to avoid "burning," are quite suitable for macroetching and involve very little expense in their preparation, saving labor and time.

4. "Etching time," i.e., time allowed for the macroetching action of the reagent, is an essential factor. Though it seems impossible to standardize exactly the necessary etching time, because of so many varying factors connected with each new specimen, it is helpful to determine the approximate minimum etching time for various steels, and use this minimum as a basis for macroetching work; the final point in the action of the reagent must depend on the completeness of developed details or of some particular characteristics, important in each given case. This is especially applicable for macroetching tests of large forgings. Approximate etching times for usual manufacturing steels, determined experimentally, are given on page 327.

5. Etching temperatures, i.e., the temperature of the reagent at which its action on the test piece is allowed to take place, is as important as etching time. Considerations of practical conditions in the technical laboratories and in the workshops (where sometimes the test has to be carried out) make it desirable to avoid troublesome exact measuring of temperature, and to select as a standard, the temperature of boiling of the reagent and to keep just at simmering point during the work to prevent excessive evaporation. Thus the control of the conditions of the bath will consist only in the observation and regulation of the boiling. The selected reagent, mentioned above, has such a composition, that boiling un-

der usual conditions of work does not change its action beyond practically satisfactory limits. Also its action is slow enough to permit such variations in "etching time" for different steels, as inevitably occur under practical circumstances.

6. The quantity of the reagent, necessary in each particular case of macroetching in practical work, depends on considerations of the chemistry of the process and of reasonable economy.

7. As seen from the above it is impossible to carry out good work in macroetching without sufficient experience. This ex-

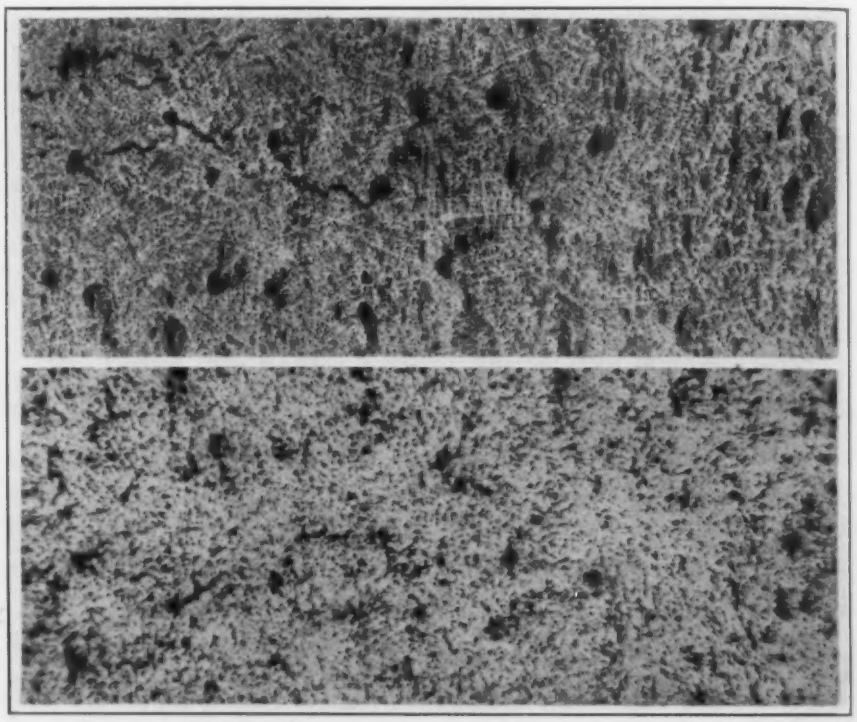


Fig. 9—Comparison of a Baumann Print with a Macroetching Picture of the Same Area, Indicating the Nature of the Pits. Macroetching Picture Above; Baumann Print Below.

perience may be acquired without particular difficulties, by a person able to appreciate important peculiarities of each case. Often, especially for large test pieces, it is impossible to use any standards of etching time, as the etching has to be started with cold pieces put in cold reagent; then experience and practical judgment of each case by its merits play a decisive role.

8. In order to be able to interpret successfully defects observed on properly macroetched pieces, there are required knowledge, experience and good judgment, not only with regard to the

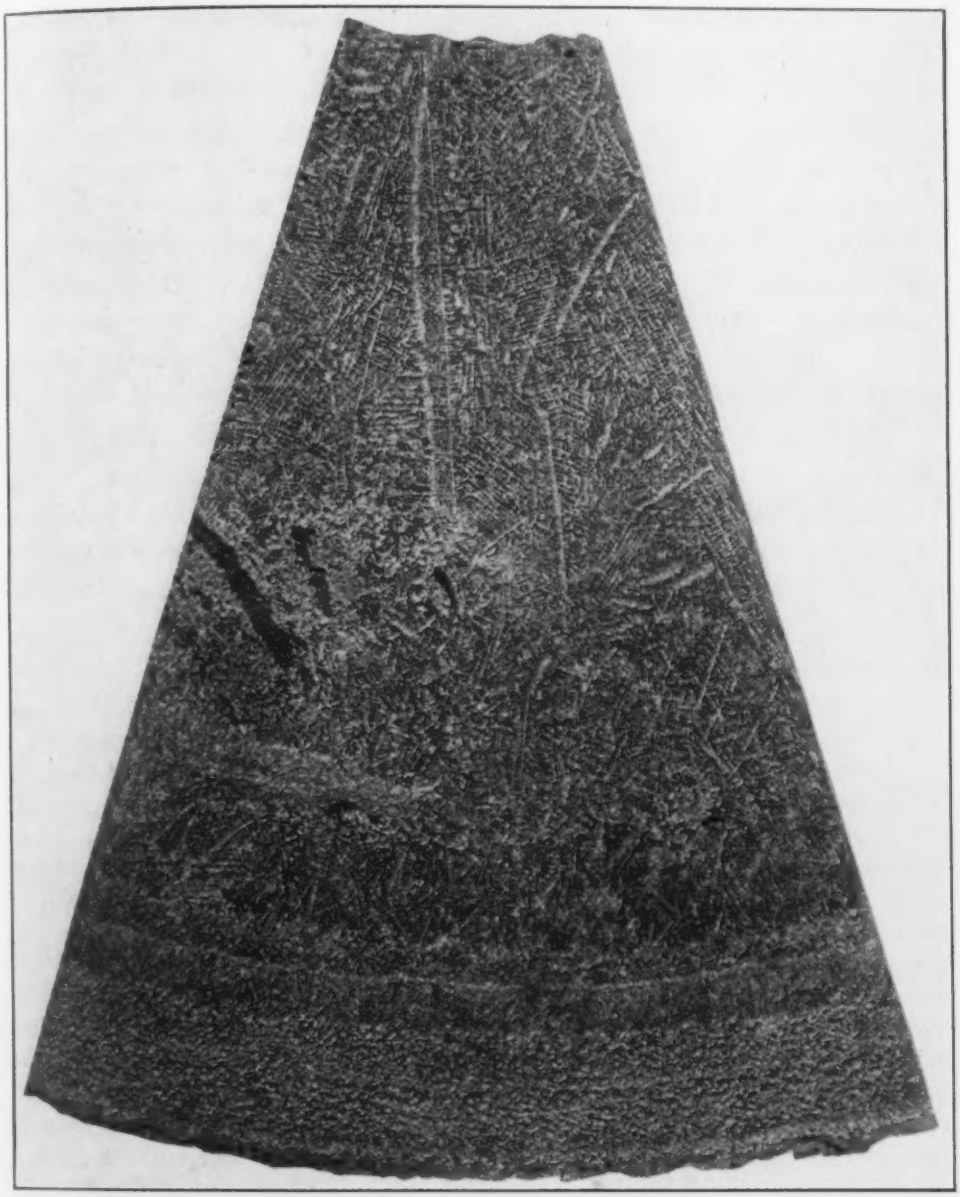


Fig. 10—Section from a Defective Centrifugal Casting Showing Segregation and Dendritic Structure. Diameter about 8½ Inches.

observation of discontinuities and nonhomogeneity in the metal, but also with regard to chemical and mechanical technology of iron and steel.

The effect obtained by macroetching with reagent C and used in accordance with the instruction of general procedure is illustrated in Figs. 9 and 10.

It is appropriate to emphasize that the investigation presented had a definite limited practical aim in view, and had no pretensions whatever to being an exhaustive or exact study of the question. It has already given beneficial practical results in the work carried on by the Arsenal, and it is hoped that it may be of some use for the steel industries outside of ordnance work.

The following acknowledgments are due in connection with this investigation; to the Ordnance Department for permission to publish this work; to Col. T. C. Dickson for his initiative and very active appreciation and deep understanding of the importance of the study of the macrostructure of metals for ordnance work; to Col. G. F. Jenks for his kindly and unreserved co-operation and help in the work; to the committee on macroetching of the American Society for Steel Treating, and particularly to their chairman, H. G. Keshian, for the information obtained from them and their co-operation; and lastly to those members of the Watertown Arsenal Laboratory staff who, by their enthusiastic work, made the investigation a practical success.

DISCUSSION

H. G. KESHIAN:[1] Dr. Yatsevitch recommends for deep etching reagent a mixture of about 10 per cent sulphuric acid, 40 per cent hydrochloric acid, 50 per cent water. That is quite different than the standard etching reagent recommended by this society. I agree with Dr. Yatsevitch that the addition of sulphuric acid actually gives a better and more distinct etched surface.

JEROME STRAUSS:[2] It occurs to me that this most interesting paper of Dr. Yatsevitch, as well as the work of the other authors upon this afternoon's program, is of itself quite incomplete. Thusfar there have been accumulated just a great fund of useful, yet purely "practical" data. Much has been said concerning the difficulty of interpretation, but obviously there can be no reliable interpretation in the absence of more fundamental facts.

We know very little, indeed, of the relative solubility in various media, under different conditions of time, temperature, etc., of sorbite, troostite, martensite and austenite of different compositions as occurring in different types of steels; nor do we have similar information concerning the behavior of the various compounds and mixtures of compounds occurring as distinct microconstituents in these steels. This applies to both carbon and alloy steels, but more particularly to the types of higher alloy content. The behavior of these several constituents, not only above, but also in contact with each other in these acid media, should also be known.

The time is opportune for a determination of the facts required for a

[1]Metallurgist, Chase Companies, Inc., Waterbury, Conn.

[2]Chief Research Engineer, Vanadium Corporation of America, Bridgeville, Pa.

full understanding of the essentials. This seems to me to be a task for a university investigation. These times have created a decrease in undergraduate and an increase in graduate registration in many of our well-equipped institutions. A carefully organized group, with units investigating individual parts of such a broad research, could within a few years establish sufficient fundamental information to permit many of the present uncertainties of hot acid etching to be dispelled. And the data collected might well lead to other important knowledge of steel behavior. Dr. Yatsevitch, as well as Messrs. Gill and Johnstin, have approached one side of this great field.

Author's Closure

I very much appreciate the kindly remarks regarding my paper, and can only regret that the lack of time prevented discussion at the meeting of many important points leading to the success of the application of the macroetching test. It does not require much imagination and insight into the metallurgy and technology of metals to realize that this method has by far greater possibilities and future than is commonly realized at present. Its development ought to be welcomed by manufacturers, perhaps, much more than by consumers, as for the latter it is only an inspection method, whereas for the former it is a tool for constructive work, giving excellent possibilities to improve methods of production and the quality of the product, and at the same time a means of educating and uplifting the consumer to a proper understanding and use of the product and thus promoting higher engineering progress in a wider sense. Materalistic considerations cannot stand in any contradiction to this point of view, as every more or less enlightened, far sighted and commercially shrewd trader knows that the most difficult and objectionable thing in business is an ignorant buyer; very often the manufacturer has to play the role of a real leader in engineering progress, bringing down to consumers the benefits of research and science. An excellent example of activities of that kind is presented in Mr. G. Luerssen's paper, which ought to be welcomed by every true engineer-metallurgist, as it gives an instance (unfortunately rare in the steel industry) of highly developed technological control of the product at all stages of its manufacture, with the *macroetching method* playing one of the important and essential parts.

With regard to Mr. Keshian's remarks about the addition of sulphuric acid to solutions of hydrochloric acid, I wish to emphasize that foreign and American literature contains many indications confirming our systematic experiments in that respect. The experience of some American steel works laboratories using our reagent is very gratifying, and I do think that the change in the recommended practice of the American Society for Steel Treating from the hydrochloric acid solution to our reagent in the proposed simplest form, as quoted by Mr. Keshian, would be of general benefit. It may be appropriate now, in view of Dr. Rawdon's remark on Mr. Keshian's paper, to point out again that for those of us who have to deal with the usual industrial conditions of mass production and haste, the group of such simple and quick acting reagents as acid solutions not involving the necessity of the preparation of finely finished surfaces, presents far greater advantages than

various copper-containing mixtures, ammonium persulphate solution, etc. Here it may also be useful to impress the value for the industry of Baumann (or so called "sulphur") printing methods. It is in reality one of the variations of the macroetching method, which may be called a *"contact macroetching method,"* because the macro-picture, produced by the chemical action of some reagent on the surface of the metal is visibly registered on suitably prepared paper, or some other medium, put in *contact with the surface.* This very valuable method is being rapidly further developed and extended, and it is not difficult to visualize this extension to cover not only the structural elements containing sulphur and phosphorus, but, possibly, all other elements as well. If such a dream-like advance in the macroetching method will come true, metallurgists will be able to study in a simple way the distribution of various elements and the complete macrostructure of metal pieces, or various parts of metallic structures without destroying them for taking samples, but just as they are. As the every day practice at the Watertown Arsenal proves the possibility and usefulness of following the macro-structure and defects on the inside and outside surfaces of guns at various stages of their manufacture by the simple application of the Baumann printing method, without the slightest damage to the work or finish, the importance of the further development of the "contact macroetching method" is realized by us most keenly.

Dr. Strauss emphasizes the necessity of having more "fundamental facts." In this way he strengthens the army of thinking metallurgists who, using the macroetching method every day, realized long ago the importance of such facts and looked for them, but could not find them, because of the generally irrational development of the iron and steel industry with regard to systematic organization and direction of research work. Therefore, in using macroetching as an inspection method in production work, we have to seek and evaluate all reliable though purely practical data. Under such conditions, quantitative experiments with various etching reagents and steels as described in the paper, seemed to me very desirable, and, as we know now, the results have borne practical fruit beyond expectations. I have to remind Dr. Strauss that a partial study of the fundamental facts on the lines indicated by him was already begun by Osmund and his students, by Heyn, Goerens, etc. The value of those fundamental facts has been realized at the Watertown Arsenal from the beginning of our studies of the macroetching method; certain preliminary studies have been made and are in progress at present. We feel, however, the impossibility of tackling the problem alone, and Dr. Strauss' suggestion of collective action of several organized groups is very welcome. Contrary to his expectations, however, it seems to me that, true to its nature and spirit, the American industry will not wait for the accomplishment of the investigations at the universities, as it can and will have the leading and decisive role itself.

In conclusion I wish to propose to establish for the test in question the term "macroetching test," and not to call it "deep etching test." The last name is quite misleading, and the first describes fully the purpose and character of the test. While the macrostructure is often developed properly only by slight etching, the deep etching is in the majority of cases not only superfluous, but undesirable for correct interpretations. Besides, the word "deep" frightens manufacturers unduly, creating prejudices against an excellent test.

ROUTINE DISK INSPECTION IN QUALITY STEEL MANUFACTURE

By G. V. Luerssen

Abstract

This paper presents the subject of deep etching from the steel maker's viewpoint. It discusses first the purpose of disk inspection, and the principles governing the choice of a workable method. It then describes in outline a routine practice currently being followed in a tool and alloy steel mill, pointing out two advantages, first, insurance to the customer against faulty steel, and second, improvement in manufacturing standards by means of closer control of operations. The paper concludes with a general discussion of the points to be considered in interpreting the test.

ONE of the outstanding features of metallurgical history during the past decade has been the increasing demand for higher and higher quality in steel products. Hand in hand with this demand has come the development of new inspection methods, particularly those designed for the detection of internal defects. Among such methods, macro-examination in its various forms has taken a very prominent place, both on account of its effectiveness as an inspection method, and because of its simplicity and economy in manipulation. Particularly has this been true of the hot acid etch test now used quite widely in the inspection of bar stock and forgings, in which cross sectional disks or slabs are cut cold and etched in hot muriatic (hydrochloric) acid.

While the method probably originated with the consumers of steel as a check upon incoming material, nevertheless the steel manufacturers made very effective use of the disk test at an early stage in its development as a check upon their own mill practice. Consequently makers of quality steels were not slow to realize the potential value of the test not only in improving their own practices, but in establishing between themselves and their customers a more definite

A paper presented before the Fourteenth Annual Convention of the Society held in Buffalo, October 3 to 7, 1932. The author, G. V. Luerssen, a member of the society, is metallurgical engineer, Carpenter Steel Co., Reading, Pa. Manuscript received July 1, 1932.

standard of quality. Co-operation between maker and consumer both in establishing the method and in laying out standards for interpretation has consequently played a very important part in the rapid development of the test.

It will be the purpose of this paper to present a side of the etch inspection question not often discussed—that seen from the viewpoint of the steel maker. Following an introductory review of the purposes of disk inspection and the principles underlying the selection of workable methods, a routine practice now in use for some years in the mill with which the writer is connected will be outlined and discussed. No attempt will be made to treat the various manipulations in a detailed manner, since the description of these is adequately covered in other papers presented to this symposium. While the practice discussed applies primarily to tool steels and the finer alloys, still it is hoped that the treatment of the subject will be sufficiently broad to cover other fields of steel manufacture.

Purpose of Disk Inspection

From the viewpoint of the steel maker the purpose of disk inspection is two-fold. Its first and most important function is to prevent the shipment of inferior material to the customer. This function becomes of extreme importance where tool steels are concerned, both on account of the heavy labor expense entailed in the manufacture of tools with consequent loss when faulty steel is encountered, and on account of the possible impairment of production schedules due to tool room delays, not to mention failures in service. A well conducted disk inspection acts as an insurance against all these contingencies. Disk inspection is likewise of great importance in connection with high grade alloy steels such as those used in aircraft, pneumatic tools, ball bearings, etc., and its advantages here are too obvious to require more than a passing comment.

The second function of disk inspection is to afford the steel maker a close and constant check upon his own manufacturing practice both in melting and in hot working. Disk inspection would never be entirely effective simply as a weeding out process. It must be made to yield information regarding the product which can be used in elevating the general standard of quality and thus to minimize final rejections. Such information can be obtained through the medium of carefully correlated records, preferably kept by order of heats.

Discussion of General Method

Any method adopted should therefore be built up around two principles, first, that of consistently supplying the customer with satisfactory material, and second, that of carrying out the method on the most economical basis possible. In general the procedure which embodies these principles most effectively is that of conducting the inspection on the semi-finished material, in the case of tool steel, on the billet.

There are many advantages in this practice. One of the most outstanding is the ability to procure results of inspection a very short time after the melting of the heat. A prompt and methodical check-up on melting practice is thus obtained, and any necessary adjustments in practice can then be made with precision. A further advantage of a prompt check-up is that it prevents the accumulation of any large quantity of questionable material in the event of some unsuspected error in practice.

A second advantage in billet inspection lies in the fact that steel can be inspected in the form of full heats. Handling in units of heats through inspection makes possible a much more comprehensive study of melting practice than is possible when heats are broken up and inspected over a wide period of time. There is the added advantage of having a more precise check upon hot working practice.

A third advantage, and one of extreme importance, is the saving in time by avoiding delays contingent upon rejecting finished material, an advantage which is quite real where definite delivery dates are to be met. There is nothing more exasperating to either manufacturer or customer, than the necessity of rejecting finished material, particularly when it is needed promptly to meet some manufacturing schedule. A final bar inspection obviously does not insure against such delays. Inspection in the billet on the other hand minimizes this hazard since it eliminates any guess work as to the quality of the material going into the finished bar.

A fourth advantage is the saving of material due to the ability of the inspector to recognize certain defects characteristic of tops or bottoms of ingots. There are some defects quite typical of the extremities of the ingot, and these can readily be eliminated by cutting back, then checking up with an additional disk. It might be mentioned here also that a more thorough inspection can be made in

billet form for the reason that defects are larger and consequently less difficult to detect.

The method as outlined presupposes that no material defects can be introduced by the final rolling or forging of the bar. Experience has proved this to be a safe assumption, the only requirement being

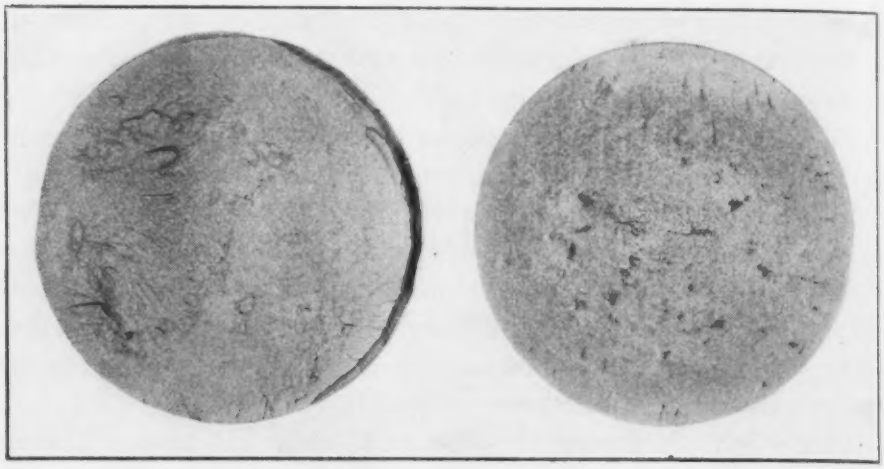


Fig. 1—(Left) Fractured Bar as Ordinarily Obtained in Usual Crop Inspection. (Right) Deep Etched Disk from Same Bar Showing Inadequacy of Crop Inspection.

that reheating temperatures and hot work practice be controlled within reasonable limits. On very large sizes it is sometimes preferable to make the inspection on the finished piece, both from the standpoint of economy, and because control of heating and final forging conditions are often somewhat difficult, and consequently in need of a final check.

It might be added that disk inspection is distinctly a test for macrostructure, and not for microstructure. Consequently whether conducted upon the billet or upon the final bar, while it detects material defects, segregation, etc., and is thus a guarantee of material quality, it is no guarantee of the annealed or treated structure, of the bar, and this can only be determined definitely by the microscope.

Description of Practice

Preparation of the Billet: Through all operations it is desirable to handle the material in units of heats. Starting with breaking down or cogging of the ingot, it is advantageous to cut as few billets as necessary. If the ingot is cut in two, the top and bottom billets are

properly marked. If the ingot is cut in three or more, the middle billet should also be identified, so that proper correlation of inspection of the billet and its location in the ingot can be made. On carbon steels over about 0.70 per cent carbon and on the harder alloy steels, it is usually necessary to anneal the billets for cutting. For this purpose a semi-anneal is sufficient, and can be carried out most rapidly in a continuous type furnace.

Cutting. Disks are usually cut on band saws or high speed hack saws. Round billets may be cut with a parting tool on a lathe or cutting-off machine. Each disk with its corresponding billet-end is stamped with the heat number together with a serial number for identification. Care is required in cutting to secure a cleanly sawed disk, and if this is done no further preparation is necessary for routine inspection. Disks cut with the parting tool may be dragged, and if so should be ground off to remove the smear of metal.

Etching. Etching is usually done in a 1:1 solution of muriatic acid in water. Duriron dishes have been found very convenient and durable, and may be heated either on an electric or gas hot plate. A thermometer is used regularly to keep etching conditions constant. The disks are etched for a prescribed time at a definite temperature depending upon the type of steel, and then scrubbed in clear water and dried with absorbent paper.

Inspection. Intelligent inspection of the disk requires not only experience and good judgment, but knowledge of melting and hot working operations, and an understanding of the physical and chemical processes underlying the various patterns developed by the etch. In other words it is necessary for the steel maker not only to determine by inspection which disk is good and which is bad; he must necessarily be able to recognize the various defects or characteristics, and classify them as to their genesis so that corrective measures may be applied when necessary. The action of acid on the various constituents must also be understood, and its tendency to magnify some of these must be recognized so that proper allowance may be made in interpreting results.

Inspection standards must be established largely through experience and knowledge of general requirements in the trade. There is of course no question concerning obvious defects such as large pits or spots resulting from inclusions, major segregations, blow holes, or center porosity and pipe. There are some characteristics developed on deep etching however which are the result of natural

processes of freezing, and consequently always present to some extent. Whether these can be considered defects or not depends upon their degree, and consequently inspection for such characteristics rests largely upon the judgment of the inspector. Principal among these are the natural increase in pitting from surface to center, development of dendrites, etc. The type of steel being inspected must be taken into account since not all steels respond alike to etching. Here again the judgment of the inspector is of great importance.

As already indicated, it is quite convenient for the inspector to classify defects under two general groups, first those which are characteristic of extreme top and bottom of the ingot, and second those which are characteristic of the entire heat. The former can be removed by cropping back until the etched disk shows the billet to be clear. This is a very beautiful and practical example of the efficacy of disk inspection, and illustrates its advantage over the former uncertain method of cropping and examining the fractured bar ends. In the case of the second type of defect however, it is necessary to approve or disapprove the entire heat upon the basis of some established standard. With proper control in melting and hot working based upon inspection data, it is possible to raise the general quality well above this standard so that loss of an entire heat becomes a rarity.

The last phase of disk inspection is that of making a final disposition of the heat and a careful record of the details of its inspection. As the inspection and cropping of each heat is completed, it is released for final rolling or forging, carrying with it a distinguishing mark to indicate that is has passed the disk test. Adequate records are of great importance, and in order to be most effective in controlling practice, are kept by heats, and submitted regularly to the operating departments interested.

Many cases are encountered in which consumers require a special type of disk inspection to meet certain peculiar conditions in their service. In such cases it is often necessary to depart somewhat from the routine method, and occasionally to make alterations in manufacturing practice to meet the special requirements. Many of the specifications encountered are quite interesting, showing how ingeniously the etch test can be employed to indicate the particular properties in which the consumer is interested. In general however it is an advantage to both consumer and maker to adhere as closely

as possible to some generally accepted standards, such as those tentatively prepared by this society.

In conclusion, the quality steel maker is striving for a perfection which he will probably never attain. Steel making is essentially a

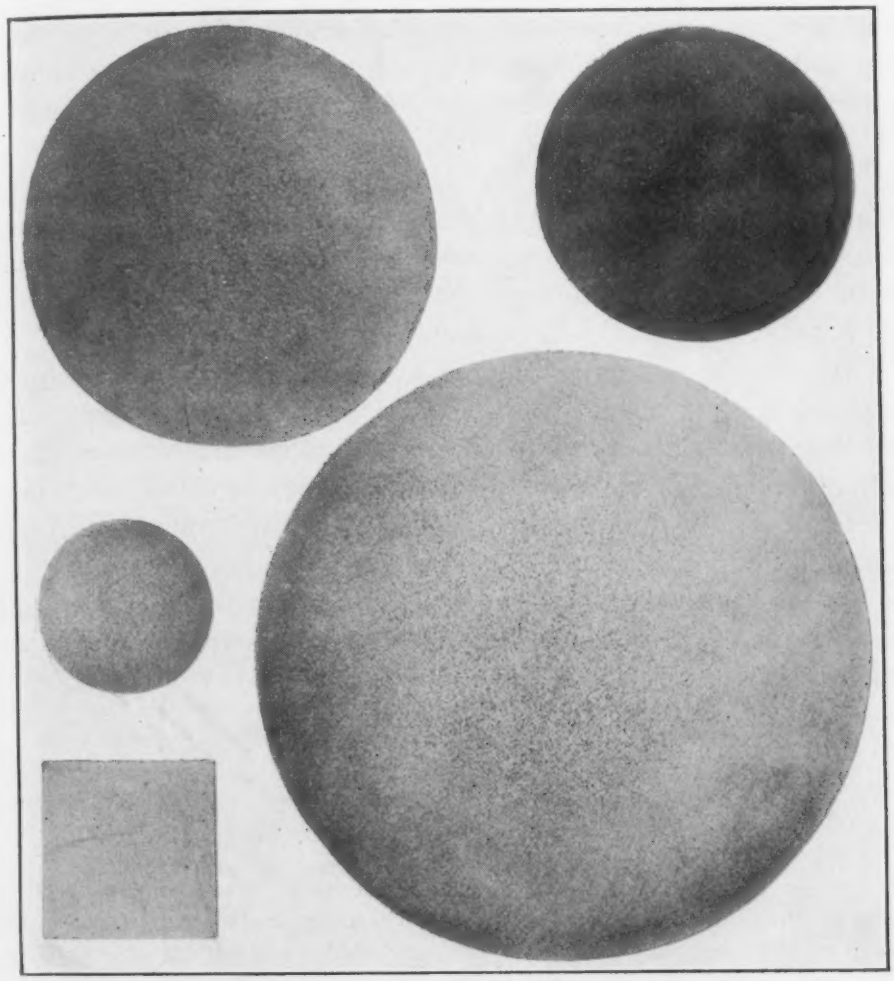


Fig. 2—Satisfactory Disks After Deep Etching. (About Actual Size.)

chemical process carried on at extremely high temperatures. Unfortunately at such temperatures the containers, that is the furnace and ladle, enter more or less actively into the reactions. Furthermore the process must be carried out in an atmosphere of nitrogen and oxygen, the latter of which combines readily with the most of the elements in the steel. Lastly the product itself, due to its chemical make-up, is of such a character that it tends to freeze, not in a

homogeneous mass like glass, but rather in a crystalline mass, and consequently subject to selective freezing of the constituents.

Thus with even the closest attention to details in melting and pouring, there are certain inherent conditions in the steel making practice, and in the process of freezing, which cannot be entirely controlled, and which will consequently under best conditions vary slightly between heats and between parts of the ingot. The acid etch is a searching test; in fact it might be said that it lays bare the very soul of the steel maker, exaggerating his shortcomings however without particularly proclaiming his virtues. Variations of a very slight order may thus be magnified by the etch so that they become not only perceptible, but often quite striking. This magnifying power, while the very thing which makes the test valuable, must be taken carefully into account when finally interpreting results.

Finally the success attained in using the test really is measured by the degree of co-operation between maker and consumer. For best results it is necessary for the maker to thoroughly understand the requirements of the user, and for the consumer on the other hand to recognize some of the more general problems encountered in steel making. Fortunately a better mutual understanding is growing year by year, and it should be a source of satisfaction to this society that the active part which it has taken in bringing forth information and establishing tentative standards for the etch test is bearing fruit.

DISCUSSION

Written Discussion: By Ralph F. Casella, assistant metallurgist, Fafnir Bearing Company, New Britain, Conn.

For the past two years, our company has inspected all raw material by means of billet inspection at the steel plant. This procedure calls for the deep etching of billet samples, taken from the top, middle and bottom of every ingot in the heat. Disks are examined under a low power binocular, and based on this as well as the severe micro-inspection for nonmetallic inclusions the heat is accepted or rejected.

There are several advantages gained by both the maker and the user. As Mr. Luerssen states, it gives the mill a constant check on their own quality, and gives the user an early opportunity to examine an entire heat of steel regardless of the final size of bar or wire manufactured. The co-operation necessary in such a method promotes a more complete understanding of the mutual problems of the user and manufacturer, resulting finally in concrete advantages for both. Any material which is not acceptable, of course, is best rejected at the earliest possible point in process. Rolling and annealing costs, for example, are saved if unsatisfactory material is rejected before these operations. We have

found the present method extremely satisfactory and one which has produced definitely discernible results for us.

Oral Discussion

NORMAN E. WOLDMAN:[1] Mr. Luerssen of the Carpenter Steel Company has presented an excellent paper on mill inspection by deep etching. It is my desire to add a few comments in favor of more complete macroscopic and microscopic examination in the rolling mill and also in the forge shop for the purpose of supplying the manufacturer of steel products a cleaner, better quality steel which is uniformly susceptible to heat treatment. It is surprising to observe the difference in quality between different shipments of steel from the one supplier, and also the large difference in quality of different shipments of steel from various suppliers. It is more surprising to observe how some heats of steel will react so abnormally to hardening in aqueous solutions.

In the deep hardening of railway and mine locomotive gears and pinions by quenching in a special aqueous solution, it is our purpose to temper back to a specified Brinell hardness of 415 to 514, holding to a close range of 444 to 477. On checking the hardness of four teeth, 90 degrees apart, of each gear, we at times find soft teeth. On further and more complete testing of the hardness of the teeth, we find that on one segment of the gear, all the teeth will have a hardness of 444 to 477 Brinell, on another segment the hardness of the teeth will be about 300 Brinell, and frequently other segments will be found with a tooth hardness of 200 to 250 Brinell. The gears will then be reannealed and rehardened with the same varying hardness, but always with some improvement. A third reannealing and rehardening will greatly improve the hardness but will still show a marked hardness variation from section to section.

On microscopic examination of transverse sections of teeth ground out from the different sections of the nonuniformly hardened gear we will always find one or more of the following defects:

(1) Banded structure showing alternate bands of low carbon and high carbon steel. Usually the low carbon bands are practically 100 per cent ferrite.

(2) Inclusion segregation in nest form or parallel bands of inclusions.

(3) Large irregular patches of free ferrite containing a small number of large inclusions or a large number of small inclusions. These patches of free ferrite can be found in the martensitic sections near the bearing faces of the tooth and also in the sorbitic-troostitic tooth core.

(4) Large spherical or elliptical patches of free ferrite containing fine inclusions, and which usually show fine hair-line cracks or ruptures. These patches are designated as goose eggs and can be seen with the naked eye as bright shiny specks on the darkened etched surface. These specks, although impossible to harden, are nevertheless harder than the adjacent steel before hardening as observed in the machining operation.

(5) Coarse dendritic structure or traces of ingotism either irregularly fashioned or uniformly fashioned in the direction of rolling or forging.

(6) Nonuniform carbon distribution.

(7) Over-oxidized steel.

[1]Metallurical engineer, materials and process engineering department, Westinghouse Electric and Manufacturing Co., East Pittsburgh.

In discussing the above points with the suppliers in question after the steel in the scrapped gears was charged back to them, the question always arose "was there not something wrong with your heat treatment, or was there not something wrong with the temperature uniformity in your furnaces?" If the heat treatment was faulty and if the temperature distribution in the furnace was bad, then the gears could be properly rehardened after the faults were corrected. But if the gears could not be rehardened then the true answer was in the steel and it was in the steel where we located 95 per cent of our heat treating troubles.

Due to the heat treating troubles we have been encountering at times from our steel suppliers, we have been forced to tighten our purchasing department specifications by adding a silicon range to the chemical analysis to better guarantee properly deoxidized steel. We have also been forced to add a range for the sum of the carbon plus manganese to guarantee the proper ratio of carbon to manganese. In addition we have been forced to add a statement that the forgings or rolled bars must be free from coarse dendrites, traces of ingotism, ferrite segregation and harmful inclusion segregation.

The above additions to the purchasing department specifications have compelled us to pay slightly higher prices for the steel. But during the past two years we have found, on close checking, that the extra costs for the better quality steel was very slight in comparison to our savings in manufacturing costs. The elimination of hard spots in the steel during machining and the elimination of heat treating troubles, rejections and scrap warranted the paying of a higher price for the steel. Furthermore, we have a better guarantee of a longer service life of our products.

If costs will permit, mill inspection cannot be overdone. But mill inspection must include more emphasis on the macro and micro-examination of the finish rolled billets. The more uniform the steel mill products, the less rigid can be the purchaser's specifications, thus enabling the elimination at least in part of these so-called extra charges for the steel.

W. H. WILLS:[2] It would be satisfactory to standardize on the testing of billets and make it a regular practice, but unfortunately there are customers who have particularly rigid specifications on deep etching in which it is necessary, in order to satisfy them, to etch the disk from the finished bar stock. This seems to be due to the fact that there may be variations throughout the length of the bar in the amount of center porosity, and also the fact that in some cases insufficient material has been cropped from the end of the bar in the finishing department inspection, resulting in off-center porosity, which of course needs to be corrected.

Author's Closure

I wish to thank Messrs. Casella, Wills and Woldman for their very helpful discussions. Mr. Casella's remarks concerning the method he employs on the inspection of billet stock is particularly interesting, since it represents a type of practice which is being successfully used on a production scale.

As Mr. Wills states there are cases in which certain customers have special requirements which necessitate a final inspection of the bar stock, and such

[2]Metallurgist, Ludlum Steel Co., Dunkirk, N. Y.

cases have been touched upon in the paper. In general, however, our experience has been that with a thorough inspection in the billet, the final bar inspection amounts to little more than a checkup, and rejection or recropping are rarely necessary.

Dr. Woldman's remarks are interesting, but somewhat beyond the field covered by the paper. In some extreme cases it is true that the deep etch test will give some indication of microstructure or even the inherent hardening characteristics of the steel. However, as a general thing it is certainly not to be recommended for determining these properties, and it is adapted primarily to detecting material defects. As noted in the paper, when microstructure is of importance the deep etch inspection should be supplemented by the microscope. For the determination of inherent hardening properties, which may be classed under the general term, "timbre," and which term really covers the various conditions so fully described by Dr. Woldman, such tests as fracture, penetration, grain size and impact are very effective, and in our experience can be applied in the inspection of material so as to prevent the various conditions which Dr. Woldman encountered in his gears.

Dr. Woldman's experience with regard to the ultimate economy in a better quality steel is noteworthy, and is in accordance with the experience of others engaged in the manufacture of quality parts.

AN INTERPRETATION OF THE DEEP ACID ETCH TEST AS APPLIED TO TOOL STEELS

By J. P. Gill and H. G. Johnstin

Abstract

This article deals with the interpretation of the deep acid etch test as specifically applied to tool steels. It discusses the effect of different acids on the structure and on the rate of solubility. It describes briefly the common characteristics which are developed by the deep acid etch and how these characteristics can be distinguished one from another. Numerous photographs are included illustrating typical examples.

THE deep acid etching of steel is constantly gaining favor as a method of inspection by the consumer and as a method of investigation by the producer. The consumer who uses the deep acid etching method for inspection is particularly interested in determining whether or not the material is satisfactory for his use. If the material is obviously defective usually the consumer is not particularly interested in the exact nature of such a defect, its probable cause and how it can be remedied. The consumer, therefore, usually interprets the deep acid etch simply as to whether or not the material is satisfactory from his viewpoint. To the producer the test is of immensely more importance as a method of investigation which when properly correlated with other tests and the microscope may give him a definite indication as to the nature of the defect and its cause. For instance, a pipe or a hammer burst means practically the same thing to most consumers but to the producer it is vital to distinguish between the two so that proper remedies can be applied. Likewise seams and cooling cracks occurring near the surface of the bar usually mean the same thing to the consumer but again it is important to the producer to distinguish between them.

Every steel is a heterogeneous mass made up of mixtures and

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors who are members of the society J. P. Gill is chief metallurgist, Vanadium-Alloys Steel Co., and Colonial Steel Co., and H. G. Johnstin is assistant metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa. Manuscript received July 1, 1932.

chemical compounds and including to a varying degree both metallic and nonmetallic segregates. Thus, all steels are subject to a selective attack by the inorganic acids commonly used for deep etching; different acids attacking different compounds or mixtures. Steels which appear solid and free of inclusions when etched with one acid may appear spongy and with many inclusions when etched with another acid. Hardened steels will etch differently than annealed steels and different alloying elements change materially the etching characteristics. To visualize these simple facts better several experiments were made comparing the solubility and selective attack of the commonly used acids—hydrochloric, nitric and sulphuric on a 1 per cent carbon tool steel and on an 18 per cent high speed steel; on hardened and annealed 18 per cent tungsten high speed steel and on a chromium-aluminum steel.

Solubility of an 18 Per Cent Tungsten High Speed Steel and of a One Per Cent Carbon Tool Steel in Hydrochloric, Nitric and Sulphuric Acids

Two steels, one an 18 per cent tungsten high speed steel and the other a 1.00 per cent carbon tool steel were selected for this experiment because one contained no alloy content and the other a very high alloy content. The choice of specimens selected for this test was based on the fact that in the standard[1] hydrochloric acid etch the high speed steel showed a pronounced degree of apparent sponginess and the carbon tool steel showed a number of small holes indicative of nonmetallic inclusions. These steels were partially dissolved in hydrochloric, nitric and sulphuric acids in both the annealed and hardened condition. The chemical composition of the two samples of steel was as follows:

High Speed Steel	Per Cent
Carbon	0.70
Tungsten	17.60
Chromium	3.81
Vanadium	0.95
Phosphorus	0.015
Sulphur	0.008
Manganese	0.25
Silicon	0.29

Carbon Tool Steel	Per Cent
Carbon	1.00
Silicon	0.27
Manganese	0.33
Phosphorus	0.017
Sulphur	0.008

[1]Standard Etch: Etch recommended by the American Society for Steel Treating is composed of 1 part commercial hydrochloric acid and 1 part water. It is used at a temperature of 160 degrees Fahr. The time of immersion for tool steels is from 30 to 45 minutes.

The high speed steel specimens which were heat treated were preheated to 1550 degrees Fahr., rapidly heated to 2340 degrees Fahr., quenched in oil and drawn at 1060 degrees Fahr. for 2 hours. The 1.00 per cent carbon tool steel samples which were heat treated were quenched in brine from 1430 degrees Fahr. and were drawn for 2 hours at 350 degrees Fahr. The specimens were machined to approximately $1\frac{3}{16}$ x $1\frac{3}{8}$ x $\frac{1}{4}$ inch and were cut adjacent to one another. Ten specimens were cut and after numbering in consecutive order as cut from the bar were subjected to the standard hydrochloric acid etch and compared in order to make certain that a similar condition existed throughout the specimen. As an additional guarantee of similarity $\frac{1}{16}$ inch was removed from the specimens which were originally etched in sulphuric and nitric acids and then etched in the standard hydrochloric acid etch to make certain that they compared with the other specimens. These tests showed conclusively that all of the specimens when etched in hydrochloric acid showed a comparable and similar condition.

All heat treated high speed steel specimens had approximately 0.020 inch removed from each surface after heat treatment, while the carbon tool steel specimens had approximately 0.010 inch removed from the surfaces after heat treatment.

All specimens were heated to a temperature of 180 degrees Fahr. in water and after reaching this temperature they were transferred to the etching solution which was at 180 degrees Fahr. and held for 30 minutes. The surfaces adjacent to those etched with hydrochloric acid were etched with nitric and sulphuric acid; consequently, these surfaces were separated in the bar only by the width of the saw cut. The photographs show surfaces of the cross section.

Table I shows the solubility results obtained by using various etching solutions, while the photographs in Fig. 1 are of the specimens which were used in this test.

A careful study of Table I and the photographs of the specimens (Fig. 1) used indicates quite clearly that these specimens should they have been etched in either nitric or sulphuric acid would have been considered excellent while etched in hydrochloric would probably have been undesirable even though the specimens etched in nitric acid lost approximately double the weight of the specimens etched in 1:1 hydrochloric acid. Are we justified in condemning a piece of steel which shows apparent sponginess when etched in hydrochloric acid and no evidence of sponginess when etched in

Table I

Solubility of Steels in Various Etching Solutions

Steel	Structure	Etching Solution By Parts Acid		By Volume Water	Weight Before	Weight After	Loss Weight	Per Cent Loss
18 Per Cent Tungsten High Speed Steel	Annealed	HCl	50	50	72.8048	68.4866	4.3182	5.9312
18 Per Cent Tungsten High Speed Steel	Heat Treated	HCl	50	50	59.3808	51.5086	7.8722	13.25
Carbon	Annealed	HCl	50	50	66.2867	62.4226	3.8641	5.82
Carbon	Heat Treated	HCl	50	50	61.4256	57.2768	4.1488	6.75
18 Per Cent Tungsten High Speed Steel	Annealed	HNO_3	25	100	72.1964	61.5619	10.6345	14.72
18 Per Cent Tungsten High Speed Steel	Heat Treated	HNO_3	25	100	59.3526	50.3026	9.05	15.20
Carbon	Annealed	HNO_3	25	100	66.4446	54.9422	11.5024	17.31
Carbon	Heat Treated	HNO_3	25	100	61.4719	51.1040	10.3679	16.86
18 Per Cent Tungsten High Speed Steel	Annealed	H_2SO_4	10	100	72.2184	69.7964	2.4220	3.35
18 Per Cent Tungsten High Speed Steel	Heat Treated	H_2SO_4	10	100	59.4252	52.1274	7.2978	12.28
Carbon	Annealed	H_2SO_4	10	100	66.7424	64.8116	1.9308	2.89
Carbon	Heat Treated	H_2SO_4	10	100	61.4470	56.6010	4.8460	7.88
18 Per Cent Tungsten High Speed Steel	Annealed	HCl	Concentrated		71.4850	66.0850	5.4000	7.55
18 Per Cent Tungsten High Speed Steel	Heat Treated	HCl	Concentrated		59.4069	50.7035	8.7034	14.65
Carbon	Annealed	HCl	Concentrated		66.2848	60.5132	5.7716	8.70
Carbon	Heat Treated	HCl	Concentrated		61.3854	55.5838	5.8016	9.45

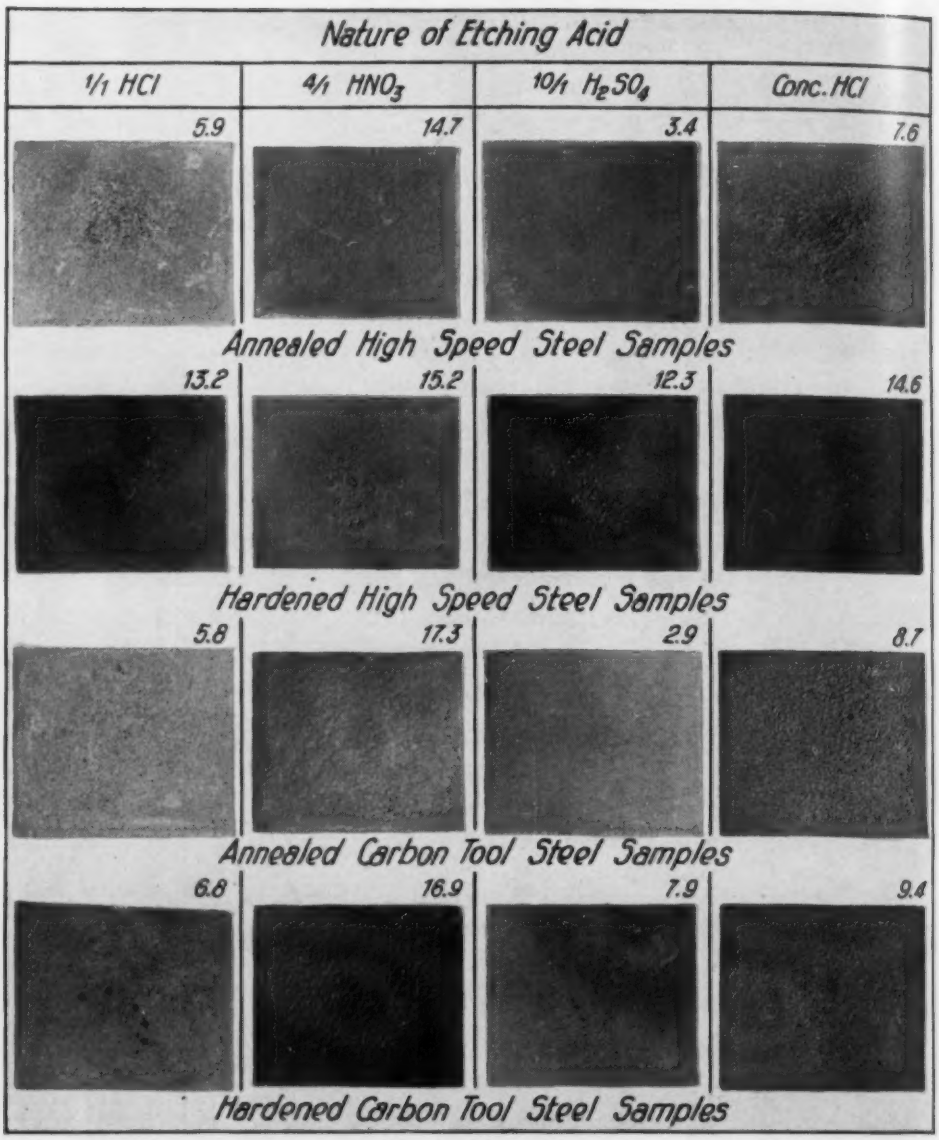


Fig. 1—Macrographs of Specimens Etched as Shown in Table I.

nitric or sulphuric acids? It is obvious that hydrochloric acid has attacked the specimens selectively to a much greater degree than either nitric or sulphuric acids even in view of the fact that the amount of steel dissolved in hydrochloric acid was between that dissolved in the nitric and sulphuric acid.

Chromium-Aluminum Steels

Examples have been given where hydrochloric acid shows a

much greater selective attack on certain types of steels. Although this may be true with the major portion of tool and special steels, nevertheless there are examples of where mixed acids will show a selective attack much more severe than will hydrochloric acid. An outstanding example of this is particularly in those steels having

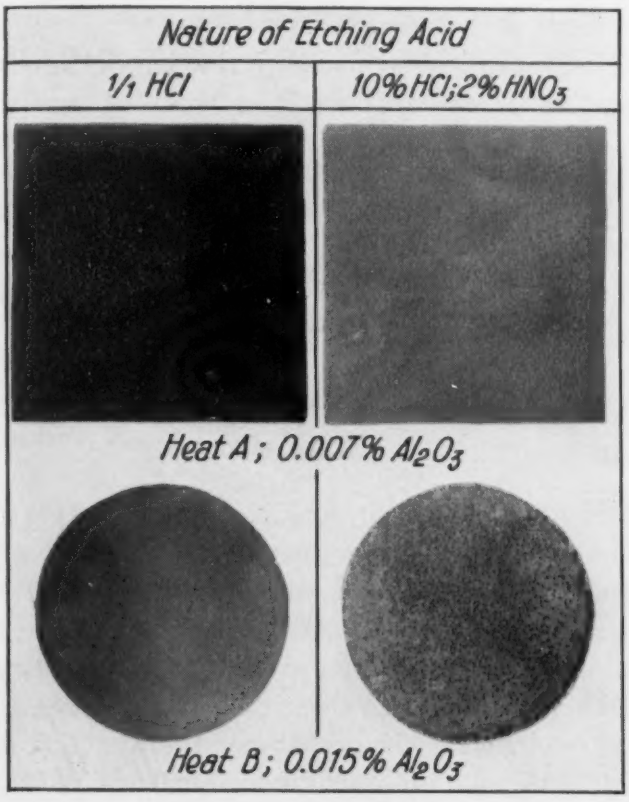


Fig. 2—Macrographs of Nitralloy Etched as Shown.

a high aluminum content. When aluminum oxide is present in these steels it is not indicated by the straight standard hydrochloric acid etch.

In the photographs of Fig. 2 are shown specimens of nitralloy of the following approximate chemical composition:

	Per Cent
Carbon	0.25
Chromium	1.40
Aluminum	1.20
Molybdenum	0.20

The specimens were taken from two heats. The photographs are

of adjacent transverse sections of one bar from each heat. One set of specimens were given an identical standard 1:1 hydrochloric acid etch, while the other set of specimens was etched for one hour at 180 degrees Fahr. in an aqueous solution[2] containing 10 per cent hydrochloric acid and 2 per cent nitric acid. A close study of these photographs makes it difficult to believe that the specimens could be of adjacent faces of the same bar.

An electrolytic analysis made by the U. S. Bureau of Mines on these samples showed that the heat from which the square bar was made contained 0.007 per cent Al_2O_3, while the heat from which the round bar was made contained 0.015 per cent Al_2O_3. This is a most excellent example of where a consumer using a standard hydrochloric acid etch would not have noted the presence of the large amount of aluminum oxides in the steel and most likely would have passed this material as desirable and satisfactory.

Hardened Versus Annealed Specimens of Steels With Metallic Segregates

The rate[3] of solubility in acid is dependent to a considerable degree upon the structural condition of the steel, that is, whether annealed, hardened or hardened and drawn. A number of references will be found in the literature showing the rate of solution on steels of the same chemical composition in different structural conditions. In highly alloyed steels such as high speed steel, ferritic stainless steels, etc., whether or not the material is in the annealed or hardened condition will vary materially the interpretation of the results. In steels which are so highly alloyed as to be of a segregated nature, such as high speed and ferritic stainless steels, etching will proceed at a greater rate at the point of contact between the segregate and the matrix. Many times the segregate will actually be etched out, leaving an apparent pit. Since usually the segregate in highly alloyed steels is not as soluble as the matrix, an examination of the etching solution when using hydrochloric acid will frequently show the presence of a finely divided black powder-like substance. Specimens of highly alloyed steels usually react to the hydrochloric acid etch much differently when hard-

[2]Solution developed by V. T. Malcom, Chapman Valve Manufacturing Co., Indian Orchard, Mass.

[3]See foot note 1.

ened, due to the fact that on hardening such steels a large part of the segregate is dissolved in the matrix and the steel is more homogeneous.

We have investigated the etching characteristics of ferritic stainless steels and other types of highly alloyed steels, such as 2 per cent carbon, 12 per cent chromium tool steels, etc., and find them to show etching characteristics very similar to the 18 per cent tungsten high speed steel. As representative of this class of materials an 18 per cent tungsten steel was selected to show the effect of structure resulting from hardening and also to prove that the pin-holes appearing particularly in the annealed specimens were the result of etching out of the segregate. Three bars of high speed steel were selected, which in the annealed condition when etched with hydrochloric acid indicated three degrees of porosity. The analyses of these specimens were substantially the same and are shown as follows:

	Per Cent					
Number	C	Si	Mn	W	Cr	V
17	0.70	0.24	0.25	17.72	4.09	0.97
18	0.67	0.28	0.28	17.60	3.93	1.00
19	0.70	0.24	0.21	17.53	4.15	0.98

Specimen number 17 was considered good, specimen number 18 intermediate and specimen number 19 spongy; this classification based on etching the annealed sample in hydrochloric acid. A close examination of specimen number 17 (Fig. 3) will show very small pits over the entire surface of the specimen. From these pits etched out a segregate which was later collected and analyzed. Our investigation showed that the apparent sponginess in specimens number 18 and 19 was chiefly the result of the segregate etching out of the specimen rather than being due to nonmetallic inclusions. The surfaces of the specimens shown in Fig. 3 were adjacent to each other, consequently, they must represent identical sections of the bar. Specimens were originally taken from 2-inch round bars, the analyses of which have already been given. They were approximately ¼ inch thick and the heat treated specimens had 0.020 inch removed from the surface after treatment. The photographs of Fig. 3 were made after subjecting the specimens to the standard hydrochloric acid etch. Sections 1¼ x 1⅜ x ¼ inch were then taken from the centers of these specimens and subjected to 21 hours at a temperature of approximately 170 degrees Fahr. in 1:1 HCl

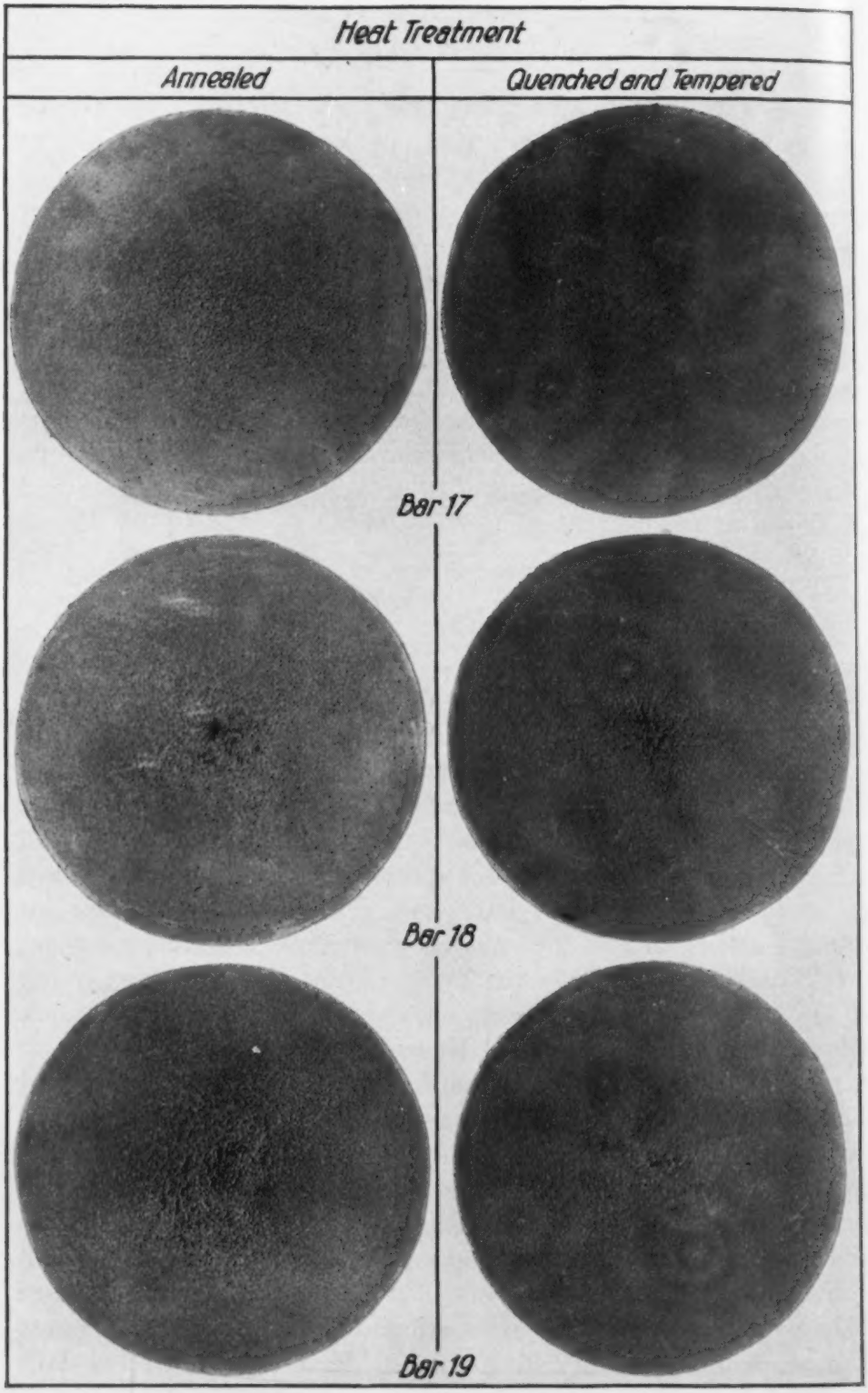


Fig. 3—Disks From 2-Inch Bars of 18 Per Cent High Speed Steel. Etched in 1:1 HCl.

Table II
Solubility of Specimens of High Speed Steel

Number Specimen	Weight Before Grams	Weight After	Loss Weight	Weight Residue	Weight Dissolved in Filtrate
A17	58.8438	24.4666	34.3773	9.2788	25.0984
A18	58.8054	28.5390	30.2664	7.8310	22.4354
A19	58.6804	22.9906	35.6898	9.3380	26.3518
T17	58.6666	7.7866	50.8800	14.2262	36.6538
T18	58.6768	10.4960	48.1808	13.4710	34.7098
T19	58.5984	1.9480	56.6504	15.5138	41.1366

Table III
Analysis of Residue of High Speed Steels of Table II

Specimen Number	Total Loss in Weight Per Cent	Weight of Residue Per Cent	Weight of Material Dissolved in Filtrate Per Cent
A17	58.42	15.76	42.65
A18	55.54	13.31	38.15
A19	60.82	15.91	44.91
T17	86.72	24.24	62.47
T18	82.11	22.95	59.15
T19	96.67	26.47	70.20

Table IV
Analysis of Residue Taken Per Gram of Residue

Specimen Number	C	W	Cr	V	Fe By Difference
A17	2.14	62.06	3.44	1.95	30.41
A18	2.22	63.40	3.26	2.26	28.88
A19	2.16	60.98	3.32	2.39	31.15
T17	1.62	60.05	2.56	1.56	34.21
T18	1.42	53.13	1.68	1.56	42.21
T19	1.52	58.29	2.42	1.70	36.07

Table V
Analysis of Filtrate Taken Per Gram of Sample Dissolved

Specimen Number	W	Cr	V
A17	0.466	3.876	0.199
A18	0.36	3.654	0.196
A19	0.62	3.844	0.136
T17	1.770	3.610	0.611
T18	1.596	4.074	0.807
T19	1.786	4.365	0.600

solution. The volume of the solution was originally 500 cubic centimeters and this volume was maintained constantly during the 21 hours by adding additional acid as needed. The residue was filtered and washed free of acid with hot water. An analysis was then made of both the residue and the filtrate.

Table II gives the solubility of the specimens, the letter "A" standing for annealed and the letter "T" for heat treated.

Table III gives the percentage of loss in weight, weight of residue and weight of dissolved material based on the original weight of specimen. Table IV gives the analysis of the residue and Table V gives the analysis of the filtrates.

The percentages as calculated in Table IV were taken on the basis of one gram sample of residue; the percentages as calculated in Table V were taken on the basis of one gram sample of the material dissolved in the filtrate. It was necessary in the case of filtrate analysis to take into account the weight of material dissolved in each case. In taking the analysis of the filtrate the following procedure was used up to the point where the elements were separated. The entire filtrate was diluted to 1000 cubic centimeters and 200 cubic centimeters each were taken for tungsten, chromium and vanadium. Calculations were made for percentages in 200 cubic centimeters, then for 1000 cubic centimeters. Knowing the weight of the material dissolved in the filtrate the percentages of each element could be calculated best on the weight of the material dissolved. It is interesting to note that the percentage of elements found in the residue of the 18 per cent tungsten high speed steel in the annealed condition corresponds closely to the percentages of carbon and tungsten as found in the double carbide of iron and tungsten represented by Westgren's formula Fe_4W_2C; the iron as found by us being somewhat lower has apparently been substituted by the chromium and vanadium present, thus forming the complex carbides of iron, tungsten, chromium and vanadium.

There is not enough difference existing between the analysis of the residues in the annealed condition of the three types to justify accounting for the difference in sponginess found. The small difference that does exist is not consistent to any degree. The differences found in the three specimens can most likely be accounted for by the degree of segregation. It is apparent that the greater the segregation the greater the selective etching, thus more apparent sponginess.

A noticeable difference does exist between the analysis of residues in the annealed and heat treated conditions. In the heat treated condition the carbon content of the residue dropped from the average 0.65 per cent, together with a drop in the other alloys present. An analysis of the filtrate in both cases shows that there is little

change in the percentage of chromium between the annealed and heat treated conditions, but that there is a considerable increase in the percentage of tungsten and vanadium as would be expected, due to the greater solubility of these elements in gamma iron. It should be noted that the heat treated samples did not etch with the same porosity as did the annealed samples, due to the solution of the segregate on hardening. It should also be noted that the degree of solubility as represented by the percentage loss in weight is not in accord with the degree of sponginess found.

Characteristic Structures and Defects

Many papers have been presented as to the characteristics and underlying causes of the structures and defects that are revealed by the deep acid etch. Usually such papers have dealt with single subjects, such as dendrites, internal cracks, nonmetallic inclusions, etc. It is obvious that a short paper dealing with the many characteristics and defects revealed by the deep acid etch can only deal generally and briefly with each.

In the recommended practice of the American Society for Steel Treating a standard etching solution is recommended, composed of one part commercial hydrochloric acid and one part water, to be used at a temperature of 160 degrees Fahr.; the steel immersed in accordance with the table printed with their recommendation. In tool steels the time recommended is from 30 to 45 minutes, according to the composition of the steel. Hydrochloric acid was selected, due to the fact that it undoubtedly has greater selective etching properties than any other single acid, and because evaporation by boiling does not change materially its concentration. In preparing specimens for photographing for this paper the recommended practice for deep acid etching of the American Society for Steel Treating was followed, except where noted.

Cracks From Etching

Highly stressed steel can be cracked by the etching solution itself. Therefore, steels in this condition should not be subjected to the deep acid etch. Unannealed, rolled or forged tool steel should not be subjected to the deep acid etch, nor should hardened tool steel, unless it has been subjected to a drawing temperature of at

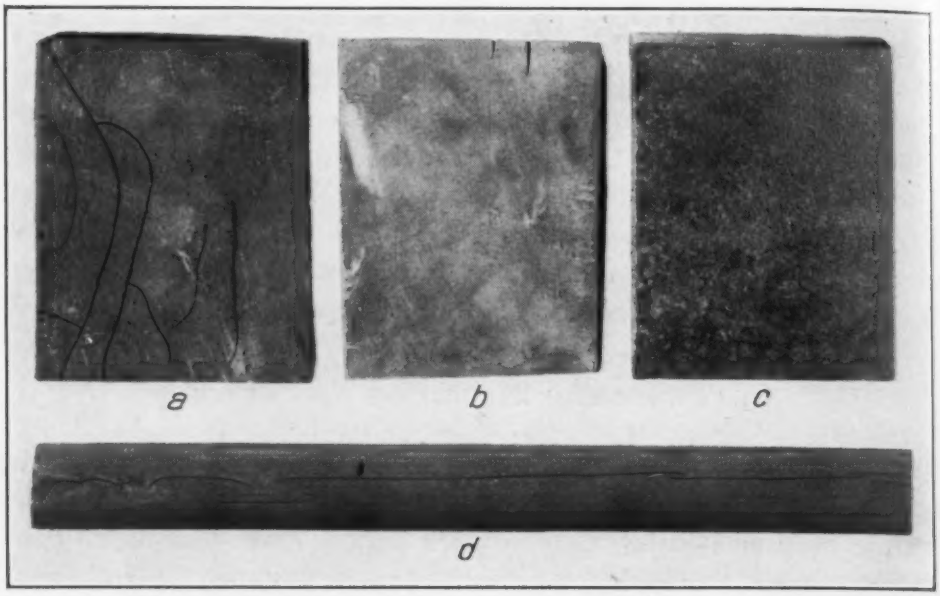


Fig. 4—(a) Oil Hardening Die Steel Cracked by Standard Etching Solution. Weight Loss 17 Grams. (b) Oil Hardening Die Steel Etched with 15 Per Cent H_2SO_4. Weight Loss 17 Grams. (c) Oil Hardening Die Steel Etched with 35 Per Cent HNO_3. Weight Loss 24 Grams. (d) Unannealed High Speed Steel Cracked by Standard Etching Solution.

least 300 degrees Fahr. for stress removal. Unannealed steels which have air hardening properties and steels whose sections are small and do not retain residual heat, are more subject to cracking from etching. Unannealed bars of steel which are sufficiently large to retain residual heat to relieve some of the stresses resulting from rolling and forging are not as susceptible to cracking in etching.

Annealed steels cannot be cracked by deep acid etching and it is difficult to crack any hardened or drawn steel in the etch if the draw has been sufficiently high to remove a part of the hardening strains. Usually a temperature of 300 degrees Fahr. is sufficiently high for this purpose. Hydrochloric acid will crack hardened and undrawn steel or unannealed steel more easily than will either nitric or sulphuric acids.

Open Grain

For lack of a descriptive term we call the condition found in the center portion of photographs of Fig. 5 as one of "open grain." It might also be termed surface roughness and many term it sponginess. This condition is the one which has probably led to more contention between the consumer and the producer than almost any other condition revealed by the deep acid etch. Specimens which

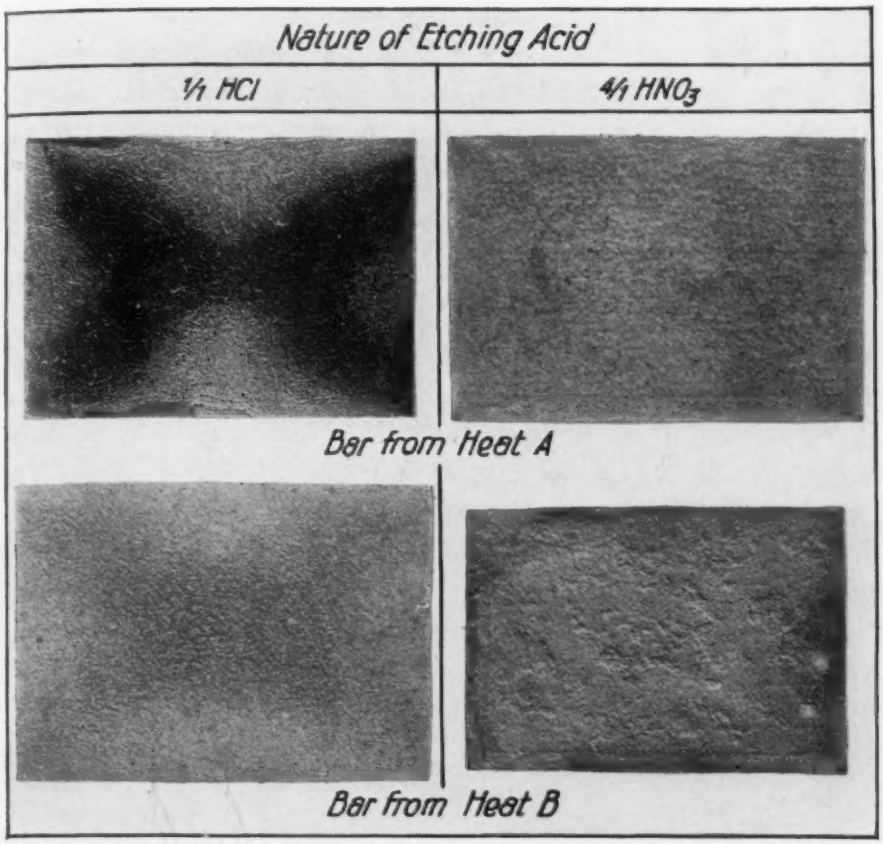


Fig. 5—Adjacent Surfaces of 2 Per Cent Tungsten Tool Steel Show Open Grain and Pattern Effect in One Acid and Etch Uniformily in Another That Does Not Attack Segregate Borders.

show this condition when etched in hydrochloric acid do not show it when etched in nitric or sulphuric acids. Such a condition, therefore, does not represent a discontinuity within the metal, but is the result of the selective etching of hydrochloric acid, as will be explained. Such a condition is controllable within certain limits by the ingot size, thickness of mold wall and casting temperature, while the deoxidizers used will vary the condition.

As the ingot solidifies columnar crystals form perpendicularly to the mold wall and these will extend inward until the temperature of the interior of the ingot has reached the solidification point. Thus, if the steel is cast "hot" the columnar crystals may reach almost to the center of the ingot, while if the steel is cast "cold" the columnar structure may reach only a short distance inward before the remainder of the steel has reached the solidification point. When an ingot of steel solidifies almost simultaneously, the crys-

tals formed are granular, while with progressive solidification the crystals formed are of a columnar nature. Columnar crystals have a tendency to throw inward the lower melting segregates, such as the sulphides and silicates, thereby concentrating them in the zone of granular crystals.

When steel solidifies, crystallization often begins around nonmetallic (oxide) nuclei. Therefore, by varying the deoxidizers and method of deoxidation there is a variation in composition, size and distribution of the oxide inclusions, many of which do act as nuclei for crystals. Because of this, steel having a high oxide content when subjected to the deep acid etch often shows a less "open grain" condition than comparatively clean steels which, having a more progressive crystallization, exhibit this characteristic. When this characteristic is in evidence it is advisable to examine the steel at low power magnification, that is, 20 to 100 diameters, in order to determine more accurately whether the steel does or does not contain an abnormal amount of nonmetallic sulphides or silicate inclusions. If such are not present in an abnormal amount, the steel should be considered satisfactory.

Pipes and Hammer Bursts

It is usually not necessary to subject steel to the deep acid etch to develop pipes and hammer bursts, as both are usually visible without etching. The advantages of the deep acid etch in developing these characteristics are to distinguish between the two. Material which has burst as the result of improper forging when subjected to the deep acid etch should not show sponginess around the burst. Material which is piped (an ingot defect) is usually spongy in the area adjacent to the open pipe. Occasionally material may be so spongy in the center that it is difficult to forge without bursting, in which case forging would not be the primary difficulty.

Center Porosity

Cross sections of bars subjected to the standard etch often show a varying degree of so-called center porosity. This porosity may be the result of an actual discontinuity within the metal, in which case it is probably more proper to classify the material as piped. Usually, however, the porosity is of such a nature that it is not visible until the specimen has been subjected to the etch. In general, center

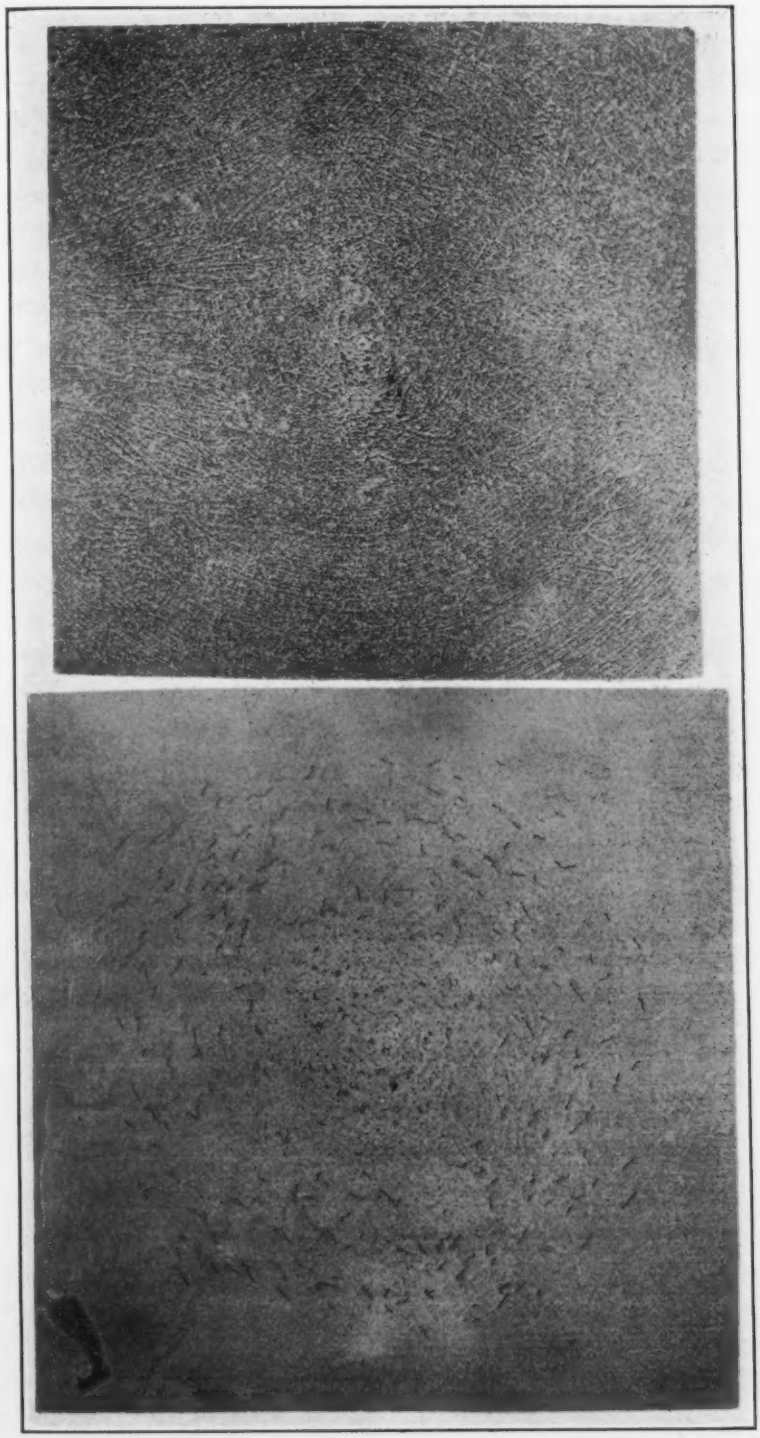


Fig. 6—Carbon Tool Steel Showing Center Porosity—Slight Standard Etch.

Fig. 7—Internal Cracks in Oil Hardening Tool Steel—Standard Etch. 10-Inch Billet.

porosity is the result of the selective etching of both metallic and nonmetallic inclusions or segregates. Crystallization of the steel in solidification throws inward those mixtures of lowest melting point and, in general, concentrates these mixtures or segregates near the center of the ingot. Such mixtures or segregates result in selective etching and will appear as holes in the steel. This condition can be found in widely varying degrees and as to whether steel showing this condition should or should not be used is usually one of experienced judgment. If the steel is to be used in a tool where the center of the bar is likely to correspond with the working portion of the tool, this condition is generally undesirable. If the material is to be used for a purpose where the outside of the bar is likely to be the working part of the tool, then this condition should be of little consequence unless it is excessive. See Figs. 6 and 7.

Unkilled Steel

Unkilled steel classed as that steel which is not fully deoxidized or degasified at the time of pouring will show numerous blow holes and nonmetallic inclusions indicative of both gases and oxides being distributed throughout the steel at the time of casting. This is readily distinguished by the deep acid etch, and is illustrated in Fig. 12.

Nonmetallic Inclusions

In killed steels nonmetallic inclusions usually appear as pits in the etched sample, consequently, should not be confused with pits occurring from the etching out of the metallic segregate. The nature of nonmetallic inclusions cannot be distinguished by the deep acid etch, although different etching reagents will probably attack differently the inclusions. Nonmetallic inclusions may be metallic oxides, silicates, or sulphides of iron, manganese or of some of the alloying elements, such as chromium. In carbon tool steels their exact nature and quantity can be determined by the electrolytic method[4] developed by the Bureau of Mines. In highly alloyed steels, in which not easily soluble alloy carbides are present, their accurate determination is not so satisfactory by the electrolytic method. When nonmetallic inclusions are suspected, or when it is

[4]Cooperative Bulletin 51 and 44, U. S. Bureau of Mines.

desirable that they be at a minimum, an etching solution,[5] made up of 10 per cent hydrochloric acid, 2 per cent nitric acid and the remainder water, is suggested, as this etching solution will develop the presence of some nonmetallic inclusions not indicated by the standard etch.

When nonmetallic inclusions are indcated in highly alloyed steels, which would contain metallic segregates or alloy carbides, then a sample of the steel should be hardened and etched for a comparison. If the pits have been caused by a metallic segregate in the annealed sample hardening will usually dissolve a sufficient amount of the segregate or carbides present, so that the hardened sample will appear much differently after the etch than the annealed sample. Etched steels containing nonmetallic inclusions appear much the same after hardening as in the annealed condition.

There are several steels in which nonmetallic inclusions are purposely formed to obtain free machining properties, such as Bessemer screw stock, in which there is considerable manganese sulphide, and in free-machining ferritic chromium stainless steels, in which there is usually considerable chromium sulphide. Nonmetallic inclusions as developed by the deep acid etch are illustrated in Fig. 1.

Metallic Segregates

All highly alloyed steels will likely contain a varying amount of metallic segregates; such segregate is usually a complex carbide having many of the characteristics of the eutectic. Often steels containing a metallic segregate will show pits when etched. These pits appear quite similar to the pits in steels having nonmetallic inclusions. Etched samples of steels containing metallic segregates can usually be distinguished from samples containing nonmetallic segregates by comparing etched samples of the steel in both the annealed and hardened states. The hardened samples will usually show fewer pits than the annealed samples if the pits have been the result of the etching out of the segregate. Usually metallic segregates will resist solution to a greater degree than the matrix, yet the point of greatest attack by the acid is the boundary between the segregate and the matrix. Samples containing metallic segregates when etched a considerable length of time (3 to 20 hours) with a standard etching solution will show a fine black powder-like substance in the solution.

[5]See foot note 2.

Metallic segregates cannot be wholly avoided, since the amount will depend primarily upon the composition of the steel, and although casting practice, such as temperature of casting, ingot size, etc., will usually vary the distribution of a metallic segregate, it does not change greatly the total amount. See Figs. 1 and 3.

Internal Cracks

Internal cracks, sometimes called flakes, chromium checks, hair line cracks or cooling cracks, can be readily observed when present by using the standard etch. The samples may be either sections taken longitudinally or transversely. These cracks are an actual discontinuity in the metal and there still exists a considerable difference of opinion as to their exact cause. In certain types of steels having some air hardening properties it appears that they are the result of the steel partially hardening when in a stressed condition, or from different areas of the steel passing through the critical range at different times whence part of the steel may be expanding, while nearby the steel may be contracting. Slow cooling will invariably overcome this condition in a large class of steels. In some classes of steels this condition is said to be essentially one of melting and the condition is said to be found in the ingots. This condition is occasionally but rarely found in carbon tool steels and will usually be found in steels having an intermediate alloy content having only slight air hardening properties. Such defects obviously make the steel unfit for use.[6]

Dendrites

Dendrites are essentially the result of the crystallization characteristics of the ingot which are not wholly eliminated in subsequent working. The standard deep acid etch will often beautifully develop a dendritic structure. The structure can be controlled partially by the casting temperature and rate of solidification of the ingot. Ordinary heat treatment will not eliminate the structure. In tool steels, in which the phosphorus and sulphur contents are very low, dendritic structure is probably of no serious consequence, since sulphides and silicates are the chief nonmetallic inclusions, the distribution of which would be likely indicated by the dendrite.

[6]See Fig. 2 of H. G. Keshian paper recorded in Reference 4 appended to this paper.

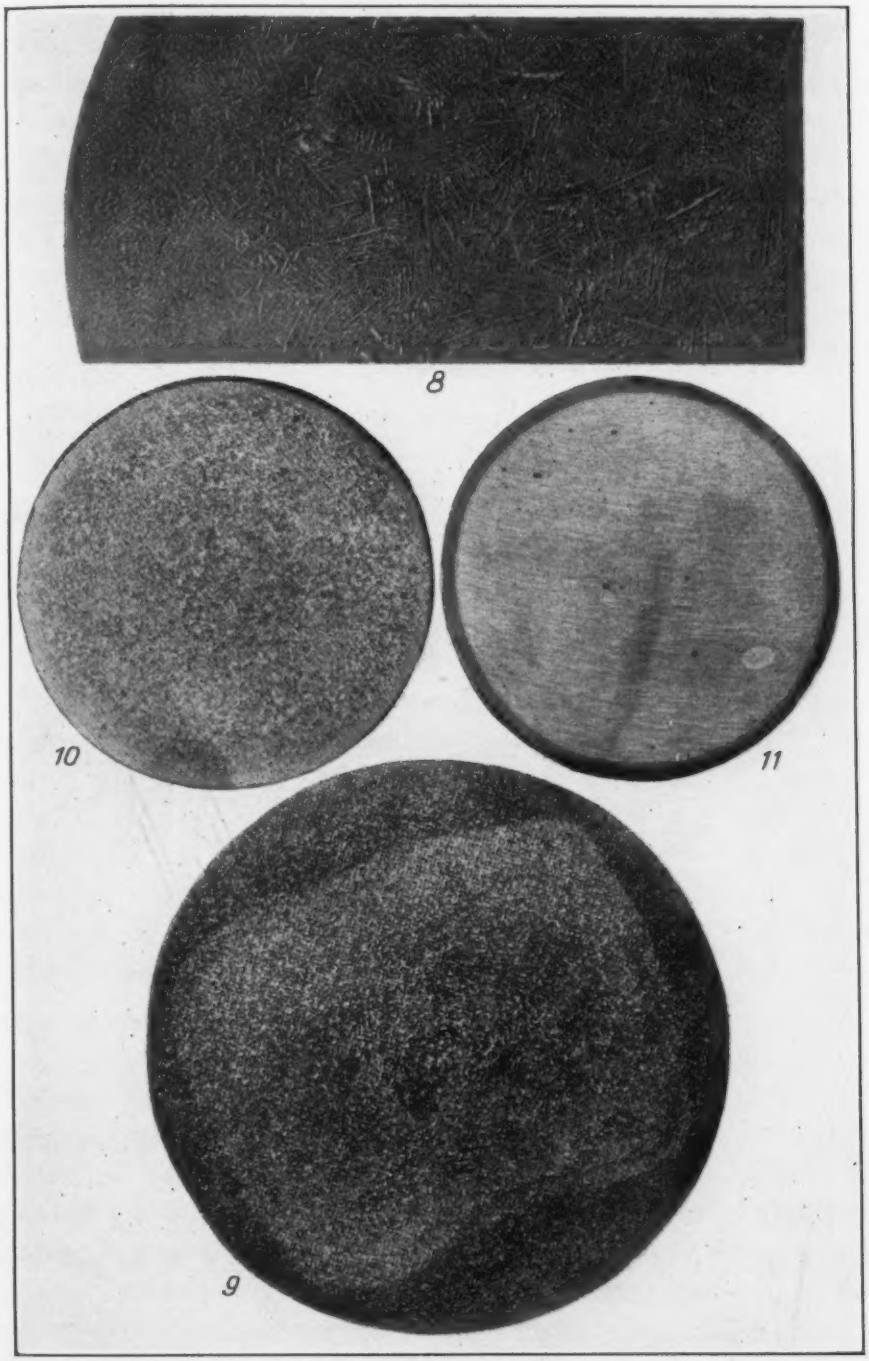


Fig. 8—Dendrites in Carbon Tool Steel. Note Absence of Oxide Inclusions. Standard Etch.

Fig. 9—Pattern Effect in Carbon Tool Steel. From Paper by Keshian, Vol. 12, TRANSACTIONS.

Fig. 10—Coarse-Grained Carbon Tool Steel. Standard Etch.

Fig. 11—Hardened 1 Per Cent Carbon Tool Steel. Etched in 5 Per Cent HNO_3 in Water for 3 Minutes.

Oxides do not follow the dendritic pattern but, on the contrary, are likely to prevent the formation of dendrites because of acting as nuclei for more simultaneous crystallization. It is significant that tool steels (usually straight carbon types) which appear highly dendritic are usually exceptionally clean and free of oxide inclusions. Carbon tool steels showing little or no evidence of dendrites are likely to contain more oxide inclusions than dendritic steels. Keshian did not find material difference in service results in comparing steels which showed heavy dendritic patterns with steels showing little or no dendritic pattern.[7] See Fig. 8.

Pattern Effect

This term is applied to the general structure in which the deep acid etch reacts differently on different sections of the same sample, thereby developing a pattern of some symmetry. The pattern effect is almost wholly the result of the crystallization characteristics of the ingot and is usually the result of that part of the bar which was the columnar structure of the ingot etching differently from that part of the bar which was the granular structure of the ingot. There is often a concentration of sulphides and silicates in the area of contact between the columnar structure and the granular structure in the ingot which is strikingly noticeable in certain samples. An example of this is illustrated by Fig. 17 of H. G. Keshian's paper,[8] which is reproduced in Fig. 9. In the absence of noticeable amounts of sulphides and silicates then the pattern effect does not show such a sharp line between the columnar and granular crystals. This will be noted by referring to Fig. 5.

Grain Size

The deep acid etch is of little or no value in determining grain size. Occasionally, however, specimens will be noted which show a mottled appearance. These specimens, upon investigation, will often show a highly enlarged grain; the mottled effect being the result of different grain orientation.

Decarburization

Decarburized areas usually etch much less rapidly than sur-

[7] See Fig. 17 of Reference 4.

[8] See Reference 4.

rounding areas and if the etch is not unduly long such areas usually are considerably lighter in color. If the specimens are subjected for too great a length of time to the acid the decarburized area will often etch in relief. In general, a mild etch will develop the decarburized area better than the standard etch.

Carburization

Carburized steels will etch in an opposite manner to decarburized steels, that is, the carburized area will usually etch darker and dissolve more rapidly in the acid. When it is desirable to contrast the carburized area with the core area a mild etch should be used.

Hardened Case

In shallow hardening steels, such as carbon and carbon-vanadium tool steels, an excellent contrast can be obtained between the case and the core by mild etching. See Fig. 11.

Flow Lines From Forging Or Rolling

Specimens which are selected for deep acid etch are usually taken of the cross section, consequently, only the ends of inclusions, segregates, etc., are visible. A section of an etched specimen taken longitudinally will show streaks and striations due to the elongating of both metallic and nonmetallic inclusions and segregates. Since all steels are heterogeneous, streaks and striations are always visible to a greater or lesser degree in a longitudinal section. Such streaks and striations are sometimes known as "flow lines," as they indicate the direction in which the steel was worked. This characteristic may prove valuable in determining whether or not a piece has been forged to shape or has been cut to shape. Flow lines in themselves do not signify defective material, since all steel regardless of its cleanliness, grain size or method of casting will show flow lines in the direction of elongation. If the striations show a high selective etching, it then may be desirable to examine the material further to determine whether or not it contains an undesirable amount of nonmetallic inclusions or metallic segregates.[9]

Surface Defects

Often the deep acid etch is used for the determination of sur-

[9]See Fig. 5, page 16, Bureau of Standards Circular 113, July 7, 1922.

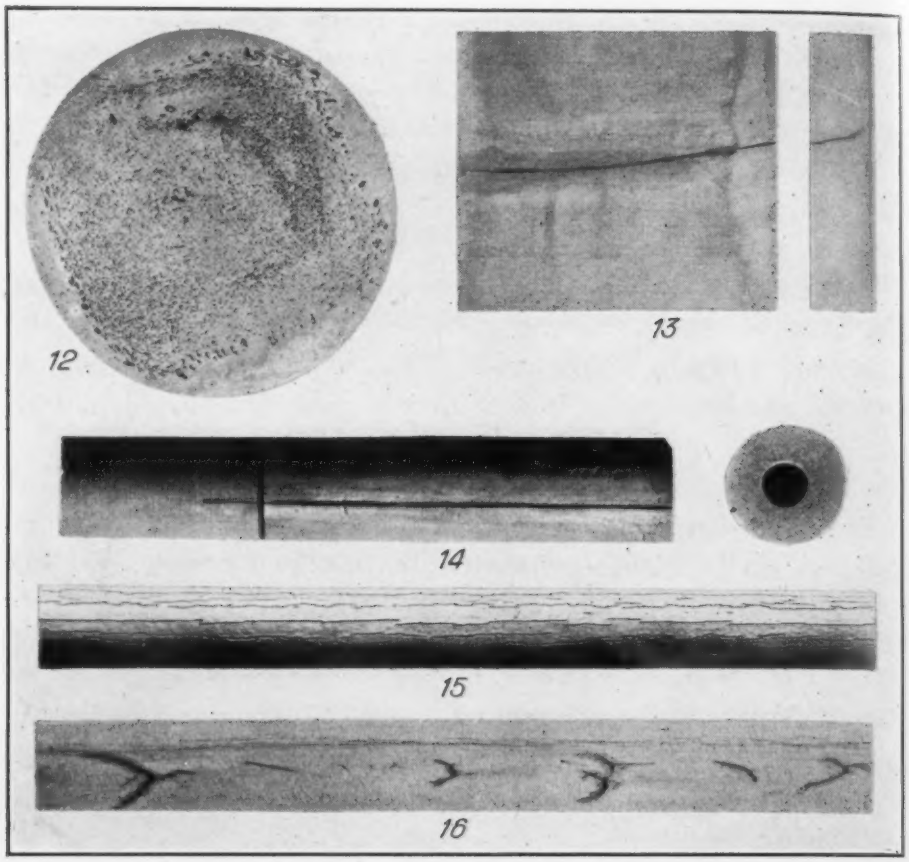


Fig. 12—Specimens of Unkilled 0.90 Per Cent Carbon Tool Steel.
Fig. 13—Cooling Crack in High Speed Steel.
Fig. 14—Seam in High Speed Steel.
Fig. 15—Cooling Cracks in Oil Hardening Die Steel.
Fig. 16—Laps in Stainless Iron Bar.

face defects. Such a method will develop defects which may not be visible otherwise. The common types of surface defects are seams, laps and cooling cracks. In general, seams can be distinguished by the fact that they are not deep and are elongated in the direction of working to a thin line. Short seams may be called "flakes." Cooling cracks are most likely to occur in self-hardening steels and can usually be distinguished by the fact that they are very deep, often reaching one-quarter or more through the bar. Occasionally cooling cracks will occur in steels other than those of the self-hardening type, in which case the cracks usually are not nearly so deep as cooling cracks occurring in self-hardening steels. Fig. 15 shows an unusual example of cooling cracks occurring in a manganese type oil hardening tool steel; these cracks resulting

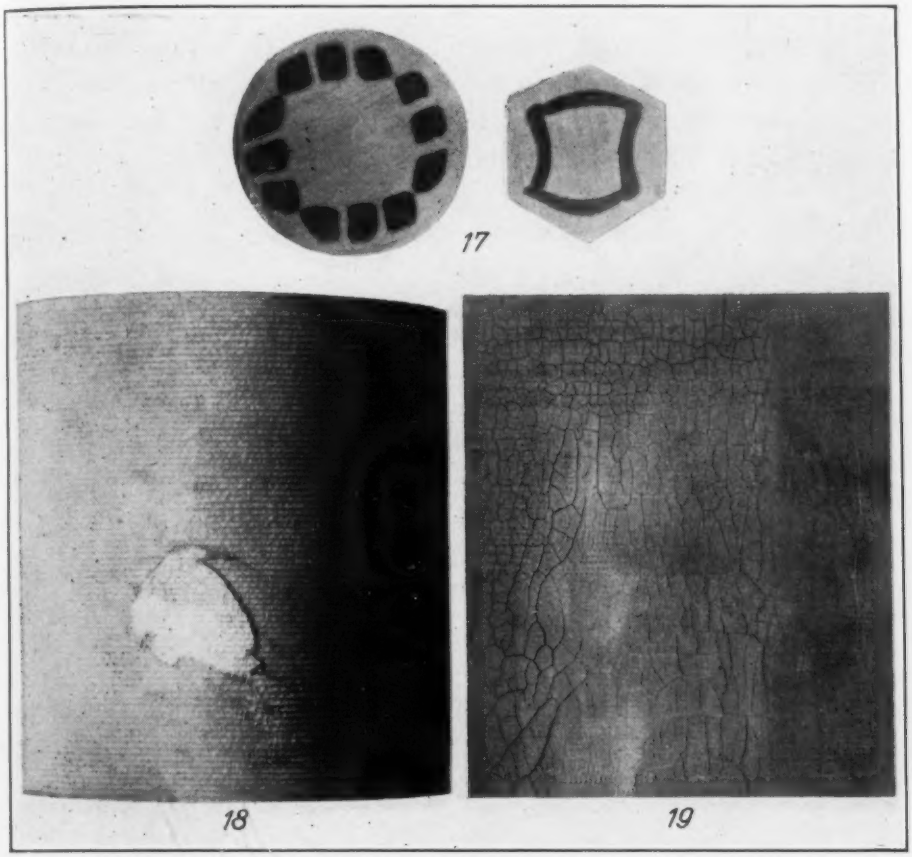


Fig. 17—Composite Steels Made Up of Hard Piles (1 Per Cent Carbon Tool Steel) and Soft Steel (0.10 Per Cent Carbon).
Fig. 18—Soft Spot in Hardened Carbon Steel.
Fig. 19—Grinding Cracks in Hardened Die Steel.

primarily from excessive decarburization, the billets having been decarburized while heating for rolling. When the bar cooled the decarburized area was contracting, while the remainder of the bar, in passing through the critical range, was expanding. This set up sufficient strains to cause excessive cracking in the surface of the bar. These cracks occurred only in the decarburized area and did not extend deeper than $\frac{1}{32}$ inch. Laps, as the term implies, is a folding over of the steel. Laps resulting from cracked billets or improperly prepared billets are usually quite obvious. Laps resulting from improper rolling can usually be distinguished from seams in the regularity of their occurrence. Illustrated in Figs. 13, 14, 15 and 16.

Soft Spots

Soft spots, which so often result in the hardening of carbon or

carbon-vanadium tool steels, can be very readily distinguished by the standard deep acid etch. The soft spots invariably etch in relief and are not so dark in color as the harder surrounding areas. The standard deep acid etch is a most excellent method for locating soft spots. This is illustrated in Fig. 18.

Composite Steels

Composite steels which may be made up of high carbon and low carbon plies and steels which may have inserts of a composition different from the surrounding material can readily be distinguished by the standard deep acid etch. See Fig. 17.

Grinding Cracks

Grinding cracks can be readily distinguished by the standard deep acid etch and are usually "ear marked" by the cracks forming a pattern of some symmetry. The fact the material contains grinding cracks does not necessarily infer that the grinding itself was improper, since most any type of steel can be so badly overheated in hardening that it will become so brittle that even the most careful grinding will cause grinding cracks to form. Illustrated in Fig. 19.

Conclusion

The deep acid etch test reveals readily and quickly many of the characteristics of steel, but in some instances the characteristics revealed require further examination by standard testing methods and the microscope to properly evaluate them. The knowledge of the fact that a piece of steel is dendritic or contains metallic or nonmetallic segregates is in itself insufficient evidence to base a definite conclusion of the properties of the material. There is real value in the deep acid etch when used to separate materials which are obviously defective from those which are not, and it has a further value in indicating characteristics which do not obviously make the material defective but which give indication that the steel should be investgated further. The deep acid etch test is one of the most simple used in the testing of steel, yet undoubtedly requires more experience and judgment to evaluate the results than any other method of testing. When used by the inexperienced it is one of the most dangerous methods of testing ever devised in that the conclu-

sions are often a matter of opinion, the value of which can be no greater than the experience and judgment of the investigator.

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DISCUSSION

Written Discussion: By W. H. Wills, metallurgist, Ludlum Steel Co., Dunkirk, N. Y.

The points brought out in the first part of this paper regarding the variation in attack of a given acid on different analyses of steel furnish a strong argument against inspection by a standardized deep etch test using one acid (such as HCl) for all grades of tool steel.

Our experience has been that this test is more applicable to the inspection of carbon, carbon-vanadium and the low alloy tool steels than to the

highly alloyed, such as high speed and the high carbon-chromium types. Deep etch tests on the latter are apt to show up unfavorably or be misinterpreted, due to the etching proceeding at a greater rate at the point of contact between the carbide segregates and the matrix. Inspection on these grades is better carried out by microscopic examination for carbide distribution and examination of hardened fractures.

The authors cover quite thoroughly the defects and characteristics of steel that are revealed by deep etching. When such etching is applied to tool steel in the hardened condition, as, for instance, to show up grinding checks or hardened case on shallow hardening steels a short time in the acid is sufficient, usually not over half the time required for annealed bar stock.

His remarks regarding "open grain" or surface roughness after deep etching might be elaborated on. This really refers to the manner of attack of the acid on the steel and we feel that there is much to be learned regarding the factors affecting it. In other words, some heats of a given analysis resist the attack of the acid to a greater extent than others. Examination of samples of the former under a low power microscope shows fewer pits than exist in the latter after the same amount of etching. This difference has been particularly noted in comparing 0.80 to 0.85 per cent carbon tool steel of open-hearth and electric furnace manufacture. The open-hearth steel lost about 4 times as much weight as the electric furnace steel when the disks were etched together for 30 minutes in 1:1 HCl. The attack of the acid on the open-hearth steel resulted in much finer and deeper pitting than on the electric furnace steel.

This condition is, perhaps, more of interest in relation to corrosion resisting steels rather than tool steels. So far as the inspection of the latter is concerned what is looked for more is nonuniformity of the attack of the acid on the disk or part under examination.

Written Discussion: By A. H. Kingsbury, Halcomb Steel Co., Syracuse, N. Y.

I have reviewed this work with a great deal of interest. I have no criticisms to offer; in fact, I consider it a very commendable paper, containing both a great deal of what appears to be scientific, as well as practical, facts.

Written Discussion: By L. A. Lanning, New Departure Mfg. Co., Bristol, Conn.

This paper by Messrs. Gill and Johnstin deserves commendation by reason of their having emphasized some of the drawbacks and inconsistencies of deep etching. They have also emphasized the necessity for good judgment in the use of this inspection method, especially as applied to judging the relative quality of tool steels.

The point with regard to the shortcomings of HCl as an etching agent for the comparatively new aluminum nitriding steels is well taken and should, perhaps, receive attention from the Recommended Practice Committee.

I believe it has been generally recognized that differences in etching may be expected when comparing hardened and unhardened steels.

However, deep etching is generally confined, as an inspection test, to incoming steels usually in the annealed condition. Under such conditions similar results should be expected. Variations in annealed structures may

show differences in results, but normally we should expect reasonably uniform annealing from our tool steel suppliers.

The authors point out that the simple 1:1 HCl mixture as recommended is so selective as to etch out segregates to give an appearance of sponginess, whereas the appearance is due to segregation alone. Too much segregation in the highly alloyed materials is also undesirable, in consequence an etching solution which brings out this condition is surely of merit.

The interpretation of an etch test must in the last analysis reflect the judgment and experience of the operator. He must learn that certain analyses may etch differently than others and to correlate these differences with the intended service of the material.

The question of bars showing center porosity is an open one in the average factory. Where a plant is engaged in the small tool business it may be possible to select bars for specific jobs where the porous section is to be removed. Very often in the shop where the tool room is an accessory, only a portion of a bar may be used for a given job. The remainder of the bar goes into storage until wanted. The first job called for boring out the center portion, but the next may involve severe duty at the center.

It becomes almost a necessity for the average plant to demand freedom from porosity at the bar center because of the above conditions, otherwise the stock room will soon accumulate a variety of bars with varying degrees of center porosity.

It becomes the duty of each plant inspector to familiarize himself with requirements and interpret his etch tests accordingly. I believe, however, that a standard mixture of acid and routine should be adhered to in order that the supplier and purchaser may thoroughly understand each others' results and interpretations.

Written Discussion: By R. W. Woodward, consulting metallurgical engineer, Hartford, Conn.

The several papers on deep etching form a very valuable contribution to our knowledge of this useful inspection method. As pointed out, considerable experience is necessary to properly interpret the results of the test. The compilation of the appearance of the most common defects given by Messrs. Gill and Johnstin will assist greatly in making a proper interpretation of such data.

Mr. Keshian wisely pointed out that the test must be carried out under uniform standard conditions. The results given by Messrs. Gill and Johnstin clearly bring out this fact insofar as the use of other than the standard HCl etch is concerned. In reading this paper the inference is gained that the authors believe because a certain bar of steel will show "apparent sponginess" when etched in hydrochloric acid and no such evidence when etched in nitric or sulphuric acid that the "apparent sponginess" does not exist and that the quality of the bar should not be questioned. They also imply that an "apparent sponginess" caused by unequal distribution of metallic segregates, rather than by nonmetallic inclusions, is not detrimental. The present writer cannot subscribe to either of these views which are rather reminiscent of the early antipathy of the seller to the deep etch test.

The use of a reagent that is selective in its action is the very founda-

tion of the deep etch test. The greater solubility reported for nitric acid merely indicates that it is attacking all constituents of the steel at nearly uniform rates.

The variation in solubility of different materials in various acids and reagents (approaching insolubility in specific cases) forms the basis of gravimetric chemical analysis and also for the etching of metals for micro-examination. For instance, in the analysis of steel for sulphur, after suitable preparation, barium chloride is added to the solution of the steel and barium sulphate, which is insoluble under the conditions present, is precipitated and by its weight the amount of sulphur in the steel determined. If sodium chloride had been added instead of barium chloride, no precipitation of sulphate would have occurred, since sodium sulphate is soluble under the conditions existing. Yet it could not be argued because a different reagent was used and no sulphate deposited that sulphur was not originally present in the steel.

Likewise, if in the micro-examination of a sample of medium carbon steel, a reagent was used for etching that failed to show any structure under the microscope, it could not be concluded that there was no pearlite in the steel.

So, in the deep etch test, if the use of *any* reagent or acid shows an "apparent sponginess" or irregularity in the distribution of some of the constituents, it must be concluded that such irregularity actually exists in the steel. Whether the irregularity observed is sufficient to condemn the steel for the use for which it is intended must be decided on the basis of prior experience with similar structures.

The three bars of high speed steel illustrated in Fig. 3 of the paper show three degrees of segregation. It cannot be disputed that bar 17 is the best of the three and should show superior results in use. It is to be expected that chemical analysis of the residues obtained from deep etching these three bars should show similar results, since they are all of similar average composition and structure. But the deep etch shows that the distribution of the metallic segregates is not the same for all, bars 18 and 19 having a greater proportion towards the center.

The writer recalls a case in which considerable trouble was experienced with slender punches shattering after short use. These punches had a large shank and were made from round bar stock of alloy tool steel. Examination of the bar stock by deep etching revealed "apparent sponginess" in the center, although of a degree that ordinarily would not be considered detrimental. Microscopic examination confirmed the fact that the segregation was of metallic segregates and not of nonmetallic inclusions. Examination of a great number of bars from several producers showed the segregation to be characteristic of the type of steel and present in a steel known to be of high quality. However, by making the punches from split rectangular bars, so that the slender punch section was offset from the original center of the bar, the shattering was overcome and normal life obtained from the tool. This would seem to prove that even a small amount of "apparent sponginess," which could not be eliminated in this type of steel by careful mill control, was detrimental for this particular use.

A. H. D'ARCAMBAL:[1] Our company learned of the so-called hot acid etch test just 12 years ago. We immediately conducted a test on all of our bars of tool steel and rejected a large number, some as large as 10 inches in diameter, due to the extreme segregation, dirt, etc., in this material as revealed through the use of this very excellent test.

I am pleased to state that today practically all of the steel that comes into our plant is very acceptable in regard to the hot acid etch test.

I might add that we have never rejected any high speed steel because of defects revealed by the hot acid etch test, due, undoubtedly, to more care being used in the manufacture of this higher quality product.

H. G. KESHIAN:[2] I would like to make one or two remarks about this valuable paper.

In discussing the nature of segregated areas as brought out by deep etching, I believe that a microstructure of suitable magnification of such areas would always prove instructive. This would have been particularly useful in the case of specimens shown in Fig. 3.

It is often necessary to determine the nature of deeply pitted condition of an etched sample. In such instances the use of the microscope will be found more convenient than the more logical chemical method used by the authors.

The authors have shown that a specimen which may show excessive segregation on deep etching may not be so bad after hardening and then deep etching the piece. This is a very important point which must be given due consideration. Whether such segregates will go into solution during heating for hardening, will of course depend first, on the nature of segregates, metallic or nonmetallic, and second, on the sufficiency of hardening temperatures to promote solubility of the segregates. The quenching temperature of all carbon and most of the alloy steels is low compared to the high quenching temperature for high speed steel; and may not be sufficiently effective to bring about the complete diffusion of soluble segregates such as carbides.

Therefore, it seems that it is much safer to aim at a steel which will show as little segregation as possible when etched in annealed state and lay little dependence on the possibility of these segregates going into solution in hardening.

E. E. THUM:[3] After Messrs. Gill and Johnstin's paper was abstracted in *Metal Progress* we received a brief communication from J. W. Weitzenkorn of Pittsburgh which I will now read.

"Some years ago I presented some 'Notes on the Manufacture of High Speed Steel' in *Chemical and Metallurgical Engineering*, March 15, 1922, in which were reported the results obtained when $\frac{1}{64}$-inch disks of high speed steel were immersed in a 10 per cent nitric acid for a long time in order to separate the carbides from the primary austenite. These old results indicate the action was as completely selective as the etching of high speed steel in 1:1 hydrochloric acid, now reported by Gill and Johnstin, as results of both investigations are in very close agreement.

[1] Pratt and Whitney Co., Hartford, Conn.

[2] Chase Companies, Inc., Waterbury, Conn.

[3] American Society for Steel Treating, Cleveland.

"The thin disks which I prepared were made from steel of somewhat similar composition to that used by Gill and Johnstin, but the portion studied was cooled very slowly from the molten state in the crucible furnace and had absorbed considerable extra carbon. Analysis showed that the carbides or insoluble residue contained approximately 56 per cent tungsten, 3.3 per cent chromium and 1.5 per cent vanadium, and that the metal in solution (originally the austenite) contained approximately 3.6 per cent tungsten, 3 per cent chromium and 0.74 per cent vanadium. These results are very similar to those reported in the paper by Gill and Johnstin.

"In my efforts a complete chemical separation of carbides was attempted, whereas Gill and Johnstin were interested in showing the effect of selective deep etching."

It would appear from this letter that both hydrochloric acid and nitric acid have a definitely selective action, and under properly controlled conditions may give us what chemists call a "quantitative separation."

It might be emphasized that the deep etch is not a test which tells all you want to know about the steel. There is enough difference of opinion as to its utility that one could immediately come to such a conclusion. Confirmation is to be had in the plant of the careful gear makers. Let me cite conditions in long use at Brown-Lipe-Chapin, Syracuse, N. Y. There you will find that the deep acid etch is only one of several tests which is used before accepting the various shipments of steel. The full list is as follows:

(a) Chemical analysis
(b) Brinell hardness
(c) Nonmetallic inclusions under the microscope
(d) Normality and grain size
(e) Deep etch to check conclusion of (c) and (d)
(f) Hardenability and fracture of disks.

This may seem an imposing list, but close co-operation between metallurgists in the gear-making plant and the steel-making plants have enabled the two to work together harmoniously. It will be observed that the last four tests mentioned must be interpreted in the light of experience. Even though one of them did not show up very well, it would be an indication that the rest of the tests for that particular shipment of steel should be scrutinized rather carefully, and not an indication that the shipment was entirely unsuitable. In other words, if the steel had proper chemistry but did not harden quite as deeply as expected, yet it had good microstructure and good deep etching characteristics, if the bars themselves had good surface, and the fracture looked good, it would certainly be unfair to reject the steel simply because the hardenability was slightly less than normal.

The same is true of good practice in the deep etch test. I think if four or five of the ordinary acceptance tests of a bar indicate good steel, the deep etch should be interpreted rather liberally.

However, if the chemistry is off and the bar does not harden very well, and if the deep etch test looks rather poor, then it is time to ask the steel maker to do something about it.

THE COBALT-TUNGSTEN SYSTEM

By W. P. Sykes

Abstract

The tentative constitutional diagram of the binary system has been constructed from data furnished by microstructures, diffraction patterns, thermal analyses and measurements of electrical resistance.

Cobalt dissolves some 35 per cent tungsten at 1465 degrees Cent. (2670 degrees Fahr.), the temperature of the eutectic. The solid solubility decreases to about 3 per cent tungsten at 550 degrees Cent. (1020 degrees Fahr.).

The complete eutectic occurs at a composition near 46 per cent tungsten and consists of the cobalt-rich solid solution (β) + an intermediate phase (δ) represented by the formula WCo (75.7 per cent tungsten). This latter phase is formed upon cooling by a peritectic reaction between the tungsten-rich solid solution (dissolving 0.2 to 0.3 per cent cobalt) and the cobalt-rich liquid.

A second intermediate phase (ϵ) forms at 1100 degrees Cent. (2010 degrees Fahr.) as the result of a peritectoid reaction between (δ) and the cobalt-rich solid solution (β). It approximates in composition the formula Co_7W_2 (47.1 per cent tungsten).

The cobalt-rich solid solutions are subject to age-hardening at temperatures above 500 degrees Cent. (930 degrees Fahr.). A maximum hardness of Rockwell C 65 (Brinell 770) has been observed as the result of aging at 600 degrees Cent. (1110 degrees Fahr.) for 200 hours a rolled alloy containing 35 per cent tungsten. The hardness developed by aging is unusually persistent at temperatures as high as 700 to 750 degrees Cent. (1290-1380 degrees Fahr.)

Introduction

FOR some time past, exploratory work in the field of certain ternary carbon-free alloys involving cobalt and tungsten, has been in progress at the Cleveland Wire Works laboratory. The data pertaining to the binary cobalt-tungsten system which is presented in

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A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, W. P. Sykes, a member of the society, is metallurgist, Cleveland Wire Works of the General Electric Co., Cleveland. Manuscript received June 16, 1932.

the following pages, have been collected in the course of these investigations.

The cobalt used in the present work was prepared in the following manner. Commercial cobalt, in the form of "rondelles" was converted to the nitrate by solution in nitric acid. The nitrate was decomposed by heating at about 600 degrees Cent. (1110 degrees Fahr.) to form the black oxide which was screened and reduced in hydrogen at 700 degrees Cent. (1290 degrees Fahr.). The resulting cobalt metal powder was used both as briquetted and sintered at 1450 degrees Cent. (2640 degrees Fahr.) in hydrogen and also in the form of melts made in alundum boats in a hydrogen atmosphere.

After the hydrogen reduction there remains in the metal about 0.5 per cent of nonmetallics, mostly alumina and silica, perhaps in the form of complex oxides containing some cobalt. By fusing the briquetted metal in an alundum container in hydrogen these nonmetallics leave the melt as a slag which, when cool, has a distinct bluish tinge. The alundum boat is noticeably attacked during the first melting operation. A second melting, however, does not affect the boat and results in a clean, sound body of metal. A typical analysis of the cobalt prepared by melting as described above is given below:

	Per Cent
Fe	0.22
Ni	0.59
Mn	0.09
SiO_2	0.05
Al_2O_3	0.01

In addition to these impurities the arc spectrum of the metal shows traces of Ca, Mg, and Cu.

In 1921 Hull[1] first described the crystal lattice of metallic cobalt. He states that X-ray diffraction patterns were made from material prepared in three different ways. The first specimens were filings taken from "very fine cobalt" furnished by Dr. H. T. Kalmus. This material presumably had been melted. The pattern was that of a perfect hexagonal close-packed lattice with no trace of the cubic form. The same filings, after annealing in hydrogen at 600 degrees Cent. (1110 degrees Fahr.) for 6 hours, showed a mixture of cubic and hexagonal close packing in about equal proportions. Hull states that

[1]A. W. Hull, "X-Ray Crystal Analysis of Thirteen Common Metals," *Physical Review* 1921, Vol. 17, p. 571.

it was not found possible by long annealing at 600 degrees Cent. (1110 degrees Fahr.) to completely change the lattice form from hexagonal to face-centered cubic. In the case of a second specimen, a fine powder obtained by reduction of cobalt oxide in hydrogen at about 600 degrees Cent. (1110 degrees Fahr.), the pattern was that of the face-centered cubic lattice with a very faint trace of the hexagonal close-packed form. A third specimen was examined which was made by dissolving a portion of the pure Kalmus cobalt (specimen #1) in sulphuric acid and electrolyzing. This showed a mixture of about equal amounts of the two forms. In Hull's data the side of the elementary cube is given as 3.554 Å, the side of the elementary prism as 2.514 Å. Density from X-ray data = 8.66. Density by standard method = 8.718.

In 1925 Matsumoto[2] reported an allotropic change in cobalt at a temperature between 403 and 477 degrees Cent. (757 and 890 degrees Fahr.). His methods included measurements of electrical resistance, thermal expansion and magnetization. He states that X-ray analysis discloses that below the transformation point the lattice is hexagonal close-packed while above this point cobalt has a face-centered cubic lattice.

Sekito[3] in 1927 investigated the structure of cobalt at room temperature and at 700 degrees Cent. (1290 degrees Fahr.). His material was purified electrolytically and melted in a Tammann furnace in hydrogen. By chemical analysis it contained 0.10 per cent iron, 0.12 per cent carbon and no nickel. The metal was forged and filed to shape before exposure to the X-ray beam. The diffraction pattern of this cobalt at room temperature contains lines of both cubic and hexagonal close-packed forms. The pattern from this metal exposed at 700 degrees Cent. (1290 degrees Fahr.) likewise shows both forms. However, from a comparison of the relative intensities of the lines Sekito concludes that at low temperatures the stable form is the hexagonal while at 700 degrees Cent. (1290 degrees Fahr.) the face-centered cubic is the stable lattice. The lattice constant for the hexagonal form is given as 2.498 Å with the axial ratio = 1.622. The lattice constant for the close-packed cubic form is reported as 3.558 Å. A specimen of this cobalt deposited electrolytically yielded the

[2] H. Matsumoto, "A New Allotropy of Cobalt," *Kinzoku no Kenku*, 1925, Vol. 2, p. 877.

[3] S. Sekito, "Lattice Constant of Metallic Cobalt," *Science Reports* of Tohoku Imperial University, 1927, Vol. 16, p. 545.

pattern of the hexagonal form only, the spacings being identical with those found in the pattern from the fused material exposed at room temperature.

More recently Hendricks, Jefferson, and Schultz[4] have investigated the lattice of cobalt metal powder formed by hydrogen reduction of the oxide Co_3O_4 throughout the temperature range from 300 to 1100 degrees Cent. (570 to 2010 degrees Fahr.). They report that the metal reduced below 400 degrees Cent. ± 20 degrees Cent. yields the pure hexagonal close-packed pattern. When the reduction temperature lies between 440 and 920 degrees Cent. (825 and 1670 degrees Fahr.) the pattern of the metal powder is that of the face-centered cubic form only. Metal reduced at 1020 ±10 degrees Cent. (1870 degrees Fahr.) and higher temperatures appeared to be made up of both cubic and hexagonal forms.

Honda[5] has shown that when cobalt is heated in a magnetic field the change in dimension passes from a negative to a positive quantity at about 470 degrees Cent. (880 degrees Fahr.) and reverses again at about 1115 degrees Cent. (2040 degrees Fahr.). He considered the latter temperature to be merely the Curie point or magnetic critical point, and to involve no change in type of lattice.

In order to confirm the existing data and to furnish a starting point for the X-ray study of cobalt-tungsten alloys the cobalt oxide Co_3O_4 was reduced in alundum boats in hydrogen at a series of temperatures ranging from 375 to 1125 degrees Cent. (707 to 2060 degrees Fahr.). The metal as reduced at 375 and 400 degrees Cent. (707 and 750 degrees Fahr.) yields a pure pattern of the hexagonal close-packed lattice. In the pattern of metal powder reduced at 450 ± 15 degrees Cent. (840 degrees Fahr.) for 100 hours the lines of both the hexagonal and face-centered cubic forms appeared. Reduction temperatures between 500 and 1000 degrees Cent. (930 and 1830 degrees Fahr.) yielded metal powders showing the pure face-centered cubic pattern. The hexagonal pattern first appeared (as one intense line and two fainter lines) along with the face-centered cubic pattern in the film from metal reduced at 1060 ± 10 degrees Cent. (1940 degrees Fahr.) and held at that temperature for three hours. Thus it appears that the transformation occurs at approximately 1020

[4]Hendricks, Jefferson and Schultz, "The Transition Temperatures of Cobalt and Nickel," *Zeit. Krist,* 1930, Vol. 73, p. 376.

[5]K. Honda, "Magnetic Properties of Matter," First Edition, p. 86.

degrees Cent. (1870 degrees Fahr.) as reported by Hendricks, Jefferson and Schultz. In the course of the present investigation several attempts were made to locate the transformation temperatures in cobalt metal by cooling curves. No positive indication of the upper point could be observed, although a relatively intense evolution of heat occurred upon cooling at about 430 degrees Cent. (805 degrees Fahr.).

By moderate deformation at room temperature the face-centered cubic form is altered wholly or in part to the hexagonal close-packed modification. When once formed the hexagonal lattice is extremely stable. Its pattern persists with but slightly lowered intensity even after heating for 200 hours at 800 to 1000 degrees Cent. (1470 to 1830 degrees Fahr.). This fact probably accounts for the many cases reported in the literature wherein the two patterns are observed to occur together. As will be mentioned later, this characteristic of cobalt renders difficult the preparation of certain alloy specimens for use in determining the composition limits of the two forms by the method of X-ray diffraction patterns.

A specimen of cobalt powder (of the approximate analysis stated previously) and reduced at 600 degrees Cent. (1110 degrees Fahr.) in hydrogen for 50 hours was examined for the writer by Dr. Kent R. Van Horn by the Hull method. The metal powder was placed in a capillary tube with a sodium chloride standard and rotated periodically during the 48-hour exposure. Calculations from the atomic spacings of eight atomic planes gave the average value of $3.51\overline{2}$ Å for the side of the elementary cube. From the hexagonal close-packed pattern obtained from the same material after grinding in a mortar the following values were obtained:

Side of elementary prism	$2.49\overline{8}$ Å
Axial ratio	$1.63\overline{1}$ Å

A second sample of cobalt powder was prepared by hydrogen reduction of ignited cobalt acetate which contained as the main impurities Fe, 0.005 per cent and Ni, 0.5 per cent. From the pattern of this metal the average value for the side of the elementary cube was $3.52\overline{2}$ Å. Using 3.512 as the edge of the unit cube the calculated value for the density of cobalt is 8.97. This figure is in fair agreement with the measured values of 8.81 to 8.36 (see Table VI) in view of the history of the specimens used in these determinations.

Values for the hardness of cobalt vary considerably with the method of preparation and the treatment. The metal powder, pressed at 30 tons per square inch and sintered 2 hours at 1400-1425 degrees Cent. (2550-2600 degrees Fahr.) has the following hardness values.

Brinell	190 to 220
Rockwell B	55 to 65
Rockwell C	8 to 10

Longer sintering with consequent increase in grain size may lower the hardness slightly. As melted and frozen in hydrogen the metal has a Brinell hardness of 130 to 140. The rate of cooling from 1400 degrees Cent. to room temperature appears to make no measurable difference in the hardness.

The metal prepared by melting as described above can be rolled or swaged cold to a limited extent before cracking. At a temperature of 800 to 1000 degrees Cent. it can be worked continuously without difficulty. The hardening rate accompanying cold rolling is shown in the following table. This metal was previously reduced 50 per cent in cross-section by hot-rolling, then annealed 15 hours at 1000 degrees Cent. After which its Brinell hardness measured 130.

The thickness at the start of the following operations was 0.250 inch. Each pass reduced the thickness by about 5 per cent.

Per Cent Reduction in Thickness	Brinell
5	175
10	200
20	230
30	270

At 20 per cent reduction several cracks appeared on the surface of the metal. One piece cold-rolled as above to a Brinell of 230 was heated at 600 degrees Cent. (1110 degrees Fahr.) for 50 hours. This treatment resulted in no softening. After 5 hours at 800 degrees Cent. (1470 degrees Fahr.) the hardness has decreased to 165 and after 25 hours at 800 degrees Cent. the Brinell hardness measured 155.

Annealing at 1000 to 1025 degrees Cent. for 20 hours or longer reduces the hardness to 130 Brinell which appears to approximate a true value for fully annealed cobalt. Kalmus and Harper[6] report a Brinell hardness of 124 for cast cobalt as cooled in the mold.

[6]Herbert T. Kalmus and C. Harper, "Physical Properties of the Metal Cobalt," *Industrial and Engineering Chemistry*, Jan., 1915, Vol. 7, No. 1, p. 6.

Constitutional Diagram

The constitutional diagram of the system cobalt-tungsten shown in Fig. 1 has been constructed from data furnished by microstructures and X-ray diffraction patterns, resistance measurements, and observation of melting points.

The greater part of the temperature measurements above 1400 degrees Cent. (2550 degrees Fahr.) were made with an optical

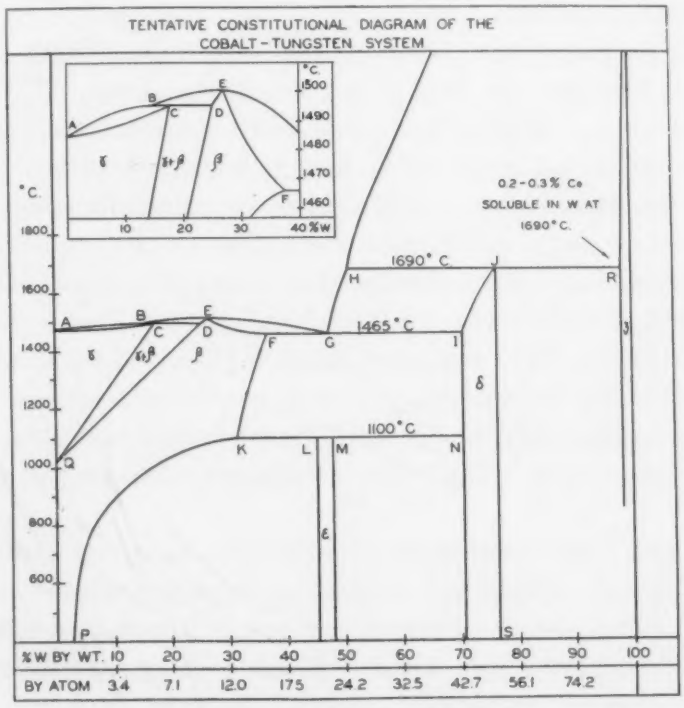


Fig. 1—Constitutional Diagram of Cobalt-Tungsten System.

pyrometer by methods previously described.[7] A rare metal couple, with potentiometer and galvanometer was used in certain instances to check the data obtained by the optical method.

All the heating at temperatures above 1000 degrees Cent. was carried out in tungsten-wound resistor furnace in a hydrogen atmosphere. By rheostat control the temperature was subject to close regulation.

For prolonged heatings at approximately constant temperature a furnace of this type was equipped with a voltage regulator operated by an automatic voltage control. A reducing valve in the hydro-

[7]W. P. Sykes, "The Iron-Tungsten System," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 73, 1926, p. 968.

gen supply line maintained the hydrogen flow through the furnace fairly constant. With such equipment the furnace was maintained at any desired temperature between 1000 and 1500 degrees Cent. (1830 and 2730 degrees Fahr.) with a variation of not more than ± 1 per cent over periods of several days.

The tungsten metal used in this investigation was in the form of hydrogen-reduced powder such as is used in the manufacture of incandescent lamp filaments. This material contains less than 0.2 per cent of impurities.

The melting point of cobalt as determined with the optical pyrometer lies between 1483 and 1489 degrees Cent. (2701 and 2712 degrees Fahr.). The freezing and melting of cobalt in a hydrogen atmosphere was followed with a thermocouple immersed in the metal. Several determinations located the melting point between 1484 and 1487 degrees Cent. (2703 and 2708 degrees Fahr.). The couple had been calibrated from the melting points of copper, 1083 degrees Cent. (1981 degrees Fahr.), nickel, 1452 degrees Cent. (2645 degrees Fahr.) and iron, 1530 degrees Cent. (2786 degrees Fahr.).

Some difficulty was experienced from super-cooling, especially when the temperature of the melt was allowed to rise much above 1500 degrees Cent. (2730 degrees Fahr.) before starting to cool the metal.

A slight rise in the melting point was observed upon the addition of tungsten. An exact determination of the solidus and liquidus throughout the range of composition up to 30 per cent tungsten was not possible with the equipment available. Melts in this composition range displayed an increasing tendency to super-cool.

By observing a series of compositions, placed side-by-side in the furnace before an alundum target and increasing the temperature above 1480 degrees Cent. (2695 degrees Fahr.) at the rate of about 1 degree Cent. per minute the relative melting points could be easily observed with the optical pyrometer. The maximum melting temperature occurs at a composition between 25 and 30 per cent tungsten. With an increase in tungsten above 30 per cent the solidus falls rapidly to 1465 ± 3 degrees Cent. (2670 degrees Fahr.) the melting point of the eutectic which is first observed at 38 per cent tungsten.

The horizontal solidus B, C, D (Fig. 1) is arrived at by the following procedure which was resorted to in an attempt to locate the direction of the solidus temperature line in this range. A series

of wires 0.025 inches in diameter were prepared by rolling, swaging, and drawing hydrogen-melted alloys. In this series the tungsten content was increased by increments of 3 per cent up to a maximum of 36 per cent. Chemical analyses of these samples indicate a maximum variation of ± 0.3 per cent tungsten from the desired composition.

After drawing to the finished size the wires were heated at 1400-1425 degrees Cent. (2550-2600 degrees Fahr.) for 15 hours in hydrogen and cooled quickly to room temperature. Short lengths of the wires including one of pure cobalt were then mounted in sets of three in holes on an alundum slab, placed in the furnace before an alundum target and heated slowly above 1480 degrees Cent. (2695 degrees Fahr.) as described above. The wires melted and fell from a vertical position at increasingly higher temperatures in the order of their increasing tungsten content until this reached 15 per cent. The wires containing from 15 to 24 per cent tungsten all appeared to melt first at the same temperature, which was determined by several separate heatings as 1495 ± 3 degrees Cent. (2725 degrees Fahr.). The wires containing 27 per cent tungsten always remained upright after all other compositions had partially melted and remained so until the temperature had reached 1503 ± 3 degrees Cent. (2737 degrees Fahr.).

Larger specimens of the worked alloys in this composition range were heated to a temperature at which liquid began to form and were then rapidly cooled. In the microstructure of such alloys containing more than 27 per cent tungsten the network of fused metal contained particles of the tungsten-rich eutectic constituent. This appeared to be quite absent in specimens containing less than 25 per cent tungsten.

Upon the basis of these data which have been procured in a somewhat unconventional manner the cobalt-rich portion of the diagram is constructed. It is probable that the location of these solidus and liquidus temperatures could be more exactly fixed by additional and more-refined methods. In view of the data furnished by the microstructures and X-ray diffraction patterns the general form of this part of the diagram appears to be reasonably correct. In the data on this system reported by Kreitz[8] the liquidus line rises to a maximum temperature of 1501 degrees Cent. (2734 degrees Fahr.) at 29.8 per cent tungsten. According to Kreitz the eutectic first ap-

[8] Karl Kreitz, "Kobalt-Wolframlegierungen," *Metall und Erz.*, Mar., 1922, Vol. XIX, No. 6, p. 137.

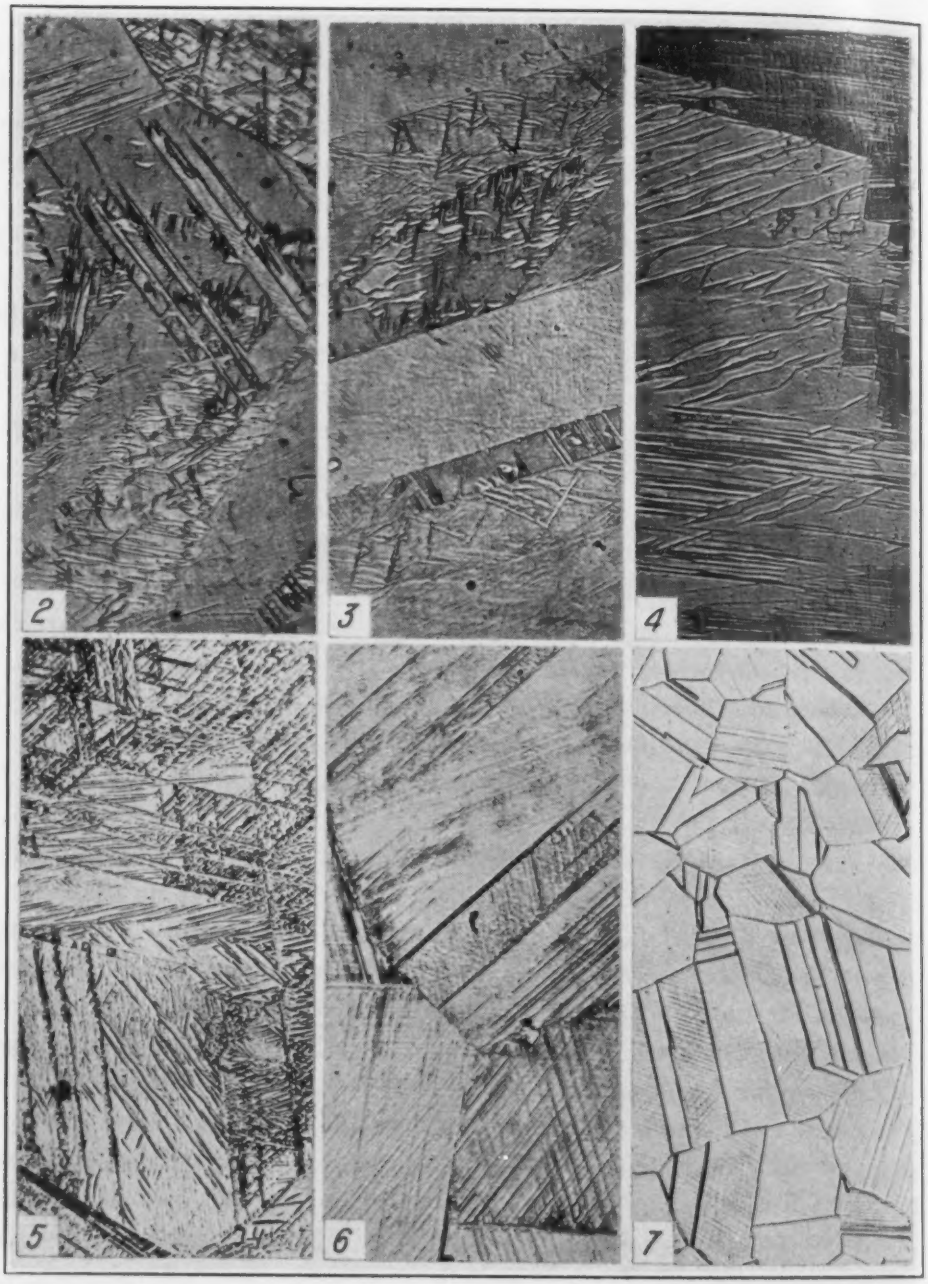


Fig. 2—Cobalt Metal. Melted and Solidified in Hydrogen; Quenched from 1400 Degrees Cent. (2550 Degrees Fahr.). × 200.

Fig. 3—Cobalt Metal. Having had same treatment as specimen in Fig. 2. × 200.

Fig. 4—Cobalt Metal. Having had same treatment as specimens in Figs. 2 and 3. × 200.

Fig. 5—Cobalt Plus 10 Per Cent Tungsten. Melted and Solidified in Hydrogen, Held 1425 ± 10 Degrees Cent. (2600 Degrees Fahr.) for 30 Minutes. Quenched. × 200.

Fig. 6—Cobalt Plus 20 Per Cent Tungsten. Having had same treatment as specimen in Fig. 5. × 100.

Fig. 7—Cobalt Plus 30 Per Cent Tungsten. Melted and Solidified in Hydrogen. Rolled and Swaged Hot and then Re-heated 1125 to 1150 Degrees Cent. (2055 to 2100 Degrees Fahr.) for 15 Hours. Quenched. × 100.

pears at 40 per cent tungsten with a melting point between 1479 to 1483 degrees Cent. (2695 to 2702 degrees Fahr.), the complete eutectic occurring at about 44 per cent tungsten. This investigator shows in his diagram a compound WCo at 75.7 per cent tungsten formed at about 1625 degrees Cent. (2960 degrees Fahr.) by a peritectic reaction between the liquid and the tungsten-rich phase.

Cobalt metal as cooled after freezing in hydrogen or after subsequent working and annealing at 1400 degrees Cent. (2550 degrees Fahr.) has a microstructure typically illustrated in Figs. 2, 3, and 4. Unless otherwise specified, the micro-sections of the cobalt-rich alloys have been etched electrolytically in a solution of equal parts hydrogen peroxide and 10 per cent HCl. A second and equally satisfactory etchant for these compositions is a solution made up of 2 parts phosphoric acid and 8 parts hydrogen peroxide.

Two types of markings are very prominent within the large polyhedral grains of the metal after polishing and etching. Blocks with straight and parallel boundaries (Fig. 3) are common in the metal both before working and after working and annealing. They resemble the twins so typical of alpha brass. Within these areas occur another set of "spindle shaped" markings (Fig. 4) similar to those described by Mathewson[9] and shown to be due to twinning in the hexagonal close-packed lattice. The formation of these twins may be associated either with (1) a partial change in lattice when cooling through the transformation temperatures, or (2) the subsequent grinding and polishing operations. As the tungsten content increases, the rectangular type of twin becomes predominant (Figs. 5, 6, 7, 8). In the microstructures of the alloys containing 30 and 35 per cent tungsten there is little indication of the second type of twin.

The alloy at 40 per cent tungsten contains an appreciable quantity of the eutectic (Fig. 9). By etching for 15 seconds in boiling sodium picrate, the tungsten-rich phase in the eutectic is darkened, while by a more prolonged etch (Fig. 10) it is completely dissolved. At a tungsten concentration of some 46 per cent the alloy appears to consist wholly of the eutectic (Fig. 11). Primary crystals of the tungsten-rich phase occur in the microstructure in alloys containing 48 per cent tungsten.

To determine the tungsten-rich terminus of the eutectic line FGI a series of alloys containing from 65 to 80 per cent tungsten

[9] C. H. Mathewson, "Twinning in Metals," *Proceedings*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1928, p. 7.

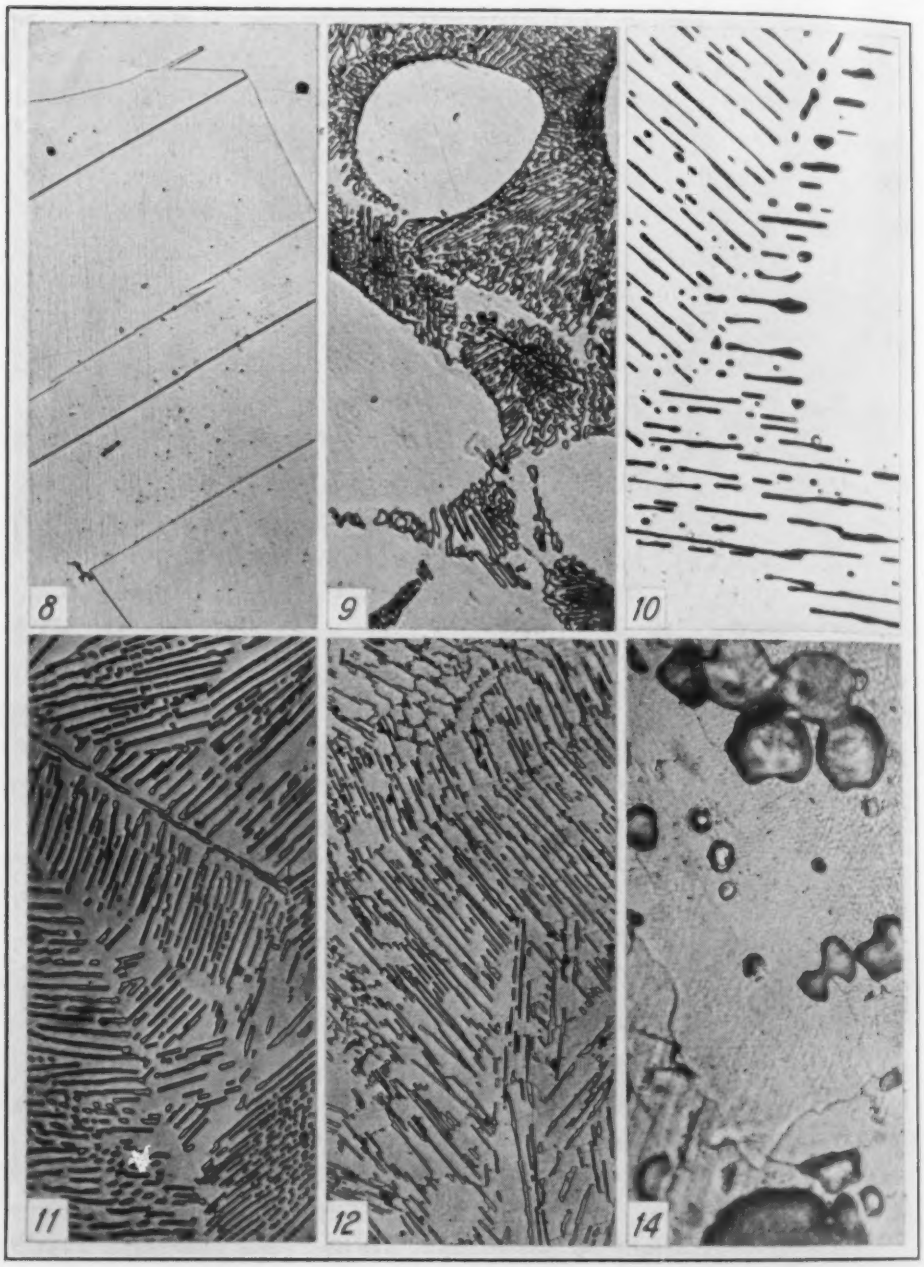


Fig. 8—Cobalt Plus 35 Per Cent Tungsten. Melted and Worked as Specimen in Fig. 7. Re-heated 1425 ± 15 Degrees Cent. for 50 Hours. Quenched. × 200.

Fig. 9—Cobalt Plus 40 Per Cent Tungsten. Melt Cooled from 1500 Degrees Cent. to Room Temperature in about 2 Minutes. × 500.

Fig. 10—Cobalt Plus 40 Per Cent Tungsten. Melt Cooled from 1500 to 1400 Degrees Cent. in 10 Minutes. Quenched. Etched in Boiling Sodium Picrate. × 500.

Fig. 11—Cobalt Plus 46 Per Cent Tungsten. Melt Cooled from 1500 to 1425 Degrees Cent. in 1 Minute. Quenched. × 500.

Fig. 12—Cobalt Plus 49 Per Cent Tungsten. Melt Cooled from 1650 to 1425 Degrees Cent. in 5 Minutes. Quenched. × 200.

Fig. 14—Cobalt 23 Per Cent, Tungsten 7 Per Cent. Pressed Powders Sintered at 1425 to 1450 Degrees Cent. for 50 Hours, 1625 to 1650 Degrees Cent. for 15 Hours. Etched Electrolytically in Solution of Equal Parts 1-N, NaOH and H_2O_2. × 500.

was prepared from the mixed and pressed metal powders by sintering at 1400 to 1425 degrees Cent. (2550 to 2600 degrees Fahr.) for 50 hours. Upon re-heating such specimens to 1470 degrees Cent. (2680 degrees Fahr.) and quenching, the presence of liquid could be detected in compositions up to 70 per cent tungsten. As the tungsten content increased above 70 per cent the solidus temperature ascended

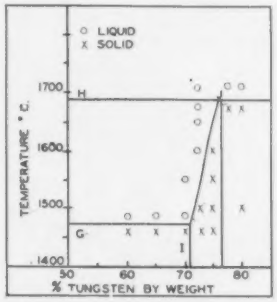


Fig. 13—Diagram Giving Detail of Solidus from 50 to 80 Per Cent Tungsten.

rapidly (see Fig. 13) to 1690 ± 5 degrees Cent. (3075 degrees Fahr.) at 76 per cent tungsten. At this temperature the intermetallic phase (marked delta in Fig. 1) decomposes into a cobalt-rich liquid and a tungsten-rich solid, this reaction being indicated in Fig. 1 by the line HJR.

Such behavior of the solidus temperature indicates that the intermediate phase is not of constant composition but extends from about 70 to 76 per cent tungsten. In Fig. 14 is shown the microstructure of this phase at the limiting composition of 76 per cent tungsten.

In solidified melts containing 55 per cent tungsten the dendrites of the tungsten-rich solid solution (Zeta phase in Fig. 1) begin to appear. These are shown in Fig. 15 as the rounded areas, and in this case have been roughened by etching electrolytically in a solution of sodium hydroxide which is the usual etch for tungsten. The lighter background in this microstructure is made up largely of the intermediate phase (delta) which has formed about the tungsten-rich centers during freezing. Some elongated primary crystals of the delta phase also can be seen which crystallized as the melt cooled from 1690 to 1465 degrees Cent. (3075 to 2670 degrees Fahr.). In Fig. 16 is reproduced the same field after a second etch in boiling sodium picrate. The delta phase has been darkened by the last

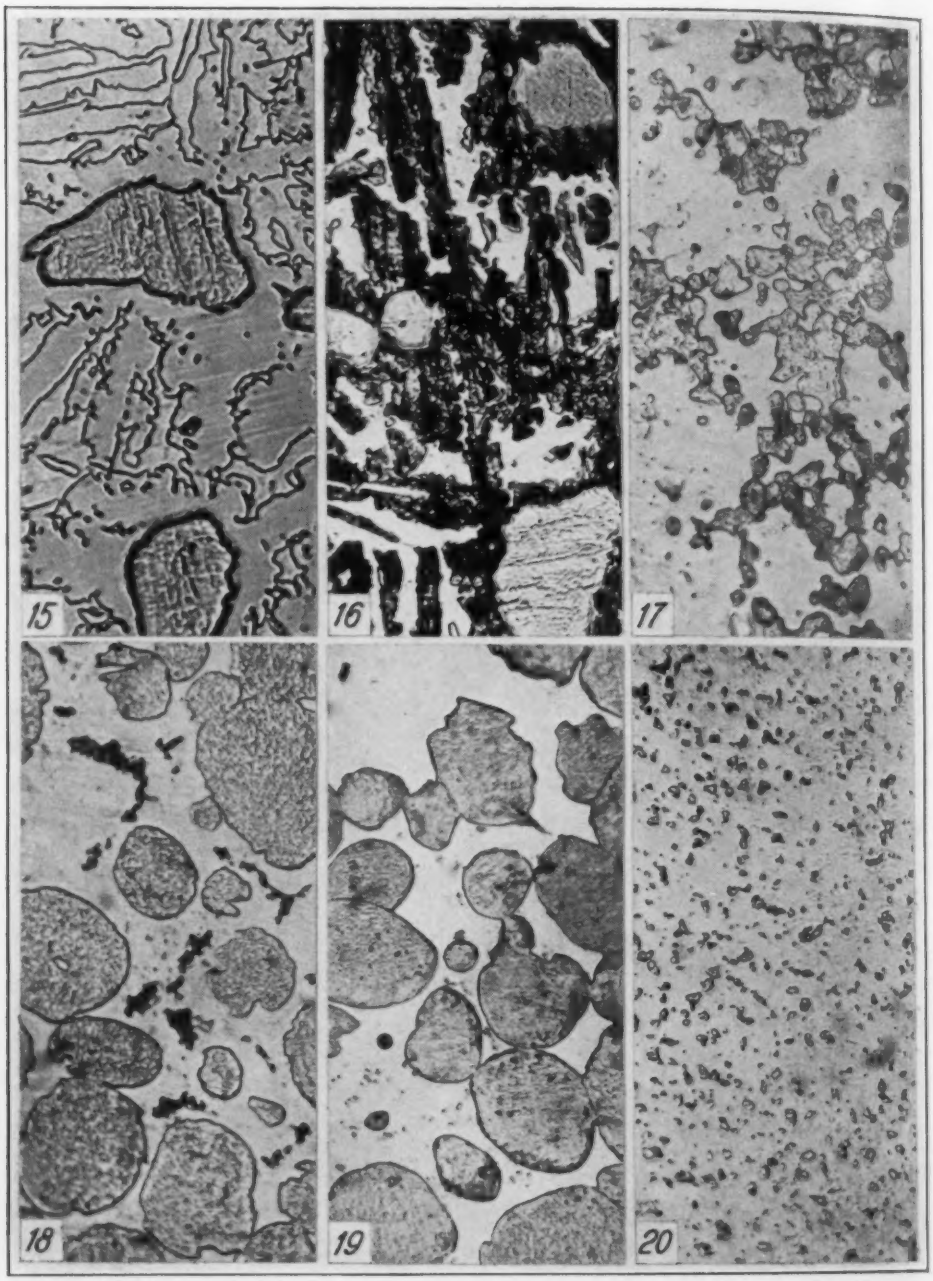


Fig. 15—Cobalt Plus 60 Per Cent Tungsten. Melted at 1800 Degrees Cent. Cooled to 1400 Degrees Cent. in 2 Minutes. Quenched. First Etch (electrolytic) 10 Per Cent HCl plus H_2O_2. Second Etch (electrolytic) NaOH plus H_2O_2. × 500.

Fig. 16—Same as Fig. 15. Third Etch, Boiling Sodium Picrate. × 500.

Fig. 17—Tungsten 85 Per Cent, Cobalt 15 Per Cent. Sintered 1450 Degrees Cent. 25 Hours. 1550 to 1600 Degrees Cent. for 25 Hours. Heated to 1650 Degrees Cent. 30 Minutes. Quenched. Etched Electrolytically in NaOH plus H_2O_2. × 500.

Fig. 18—Same as Fig. 17. Then Heated to 1700 Degrees Cent. for 5 Minutes and Cooled to Room Temperature in 2 Minutes. Etched (1) Electrolytically in 10 Per Cent HCl plus H_2O_2 (2) Electrolytically in NaOH plus H_2O_2. × 500.

Fig. 19—Same as Fig. 18 but Cooled from 1700 to 1300 Degrees Cent. in 2 Hours. Etched Electrolytically in NaOH plus H_2O_2. × 500.

Fig. 20—Tungsten 98 Per Cent, Cobalt 2 Per Cent. Sintered 1550 Degrees Cent. 25 Hours. 1550 to 1650 Degrees Cent. 25 Hours. Etched Boiling Sodium Picrate. × 500.

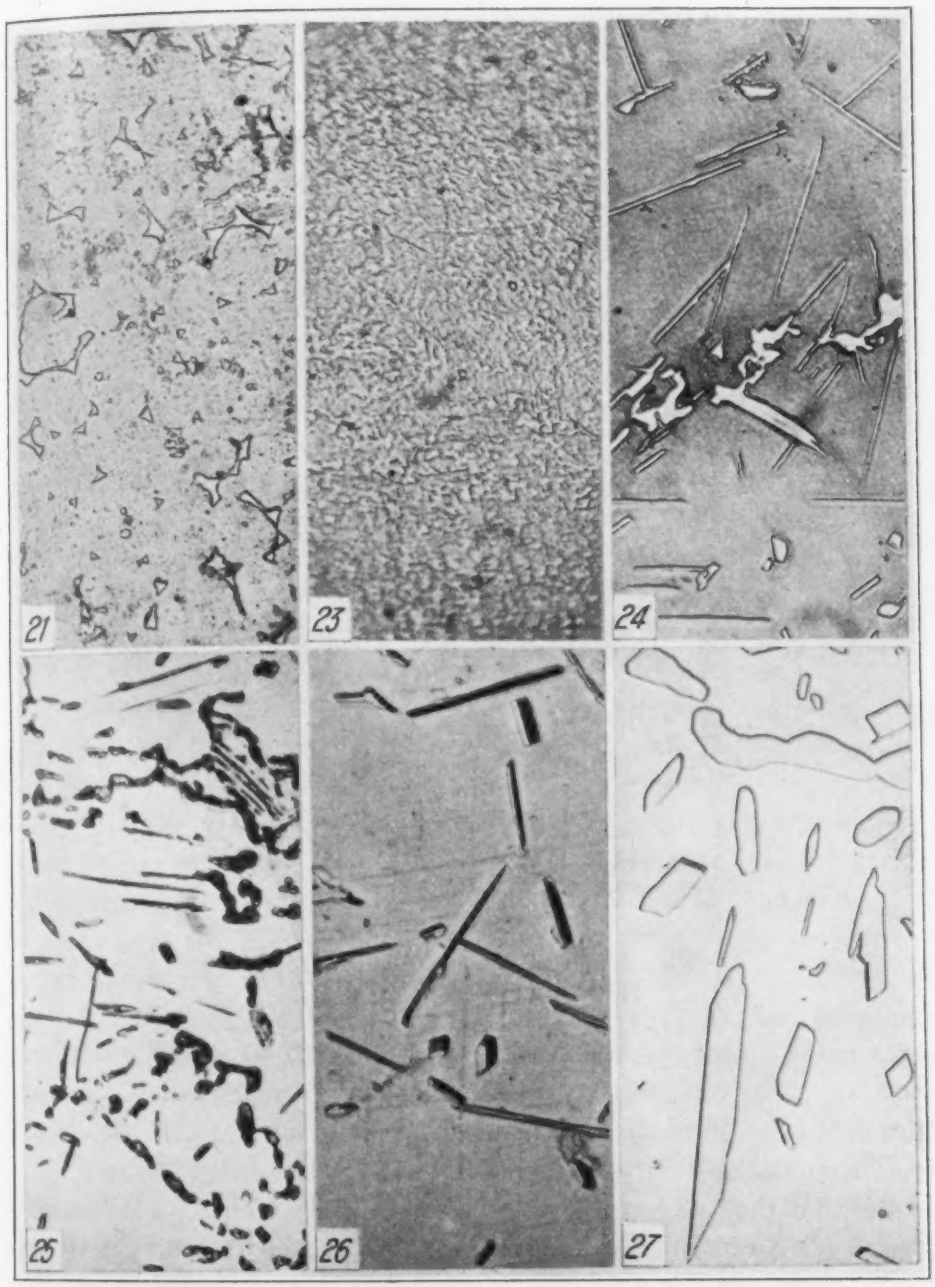


Fig. 21—Same as Fig. 20 and Subsequently Heated to 1700 Degrees Cent. for 10 Minutes. Etched Electrolytically in NaOH plus H_2O_2. × 500.

Fig. 23—Tungsten plus 0.3 Per Cent Cobalt. Treated as Specimen in Fig. 20, Etched in NaOH plus H_2O_2. × 1000.

Fig. 24—Cobalt plus 38 Per Cent Tungsten. Melt. Quenched 1425 Degrees Cent. and Re-heated 1140 ± 15 Degrees Cent. for 50 Hours. Quenched. Etched in 10 Per Cent HCl plus H_2O_2. × 700.

Fig. 25—Cobalt plus 38 Per Cent Tungsten Having Had Same Treatment as in Fig. 24. Etched in Boiling Sodium Picrate. × 700.

Fig. 26—Cobalt plus 35 Per Cent Tungsten Having Had Melt Held at 1425 Degrees Cent. for 50 Hours, 1300 Degrees Cent., 25 Hours, 1150 Degrees Cent., 25 Hours and Quenched. Etched in 10 Per Cent HCl plus H_2O_2. × 500.

Fig. 27—Cobalt plus 35 Per Cent Tungsten. Treated and Etched as Fig. 26. × 700.

etch as was noted in the description of Fig. 10. A scattering of unetched areas remains in Fig. 16 representing the last cobalt-rich liquid to solidify at 1465 degrees Cent. (2670 degrees Fahr.). As the tungsten content exceeds 76 per cent the tungsten-rich solid solution occupies an increasingly greater area in the microstructure. In Fig. 17 is shown the structure of an 85 per cent tungsten alloy formed by sintering the pressed powders of cobalt and tungsten at tempera-

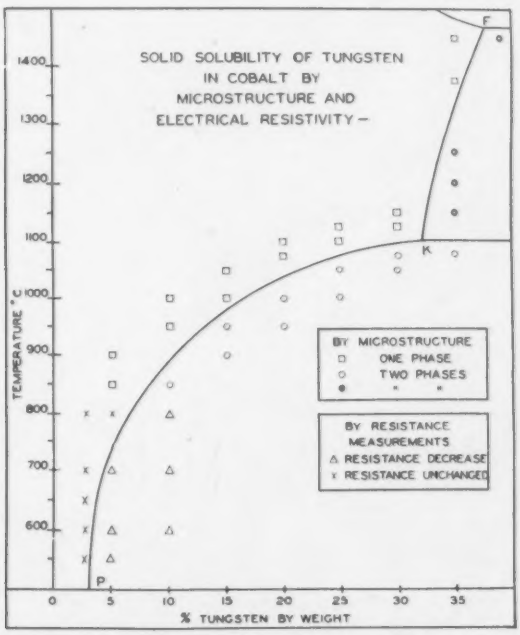


Fig. 22—Diagram Giving Detail of Solid Solubility Limits in Cobalt-Rich Field.

tures between 1450 and 1650 degrees Cent. (2640 and 3000 degrees Fahr.). The small islands of the tungsten-rich phase (darker) are here scattered through a matrix of the delta phase. No liquid has ever been formed in this specimen.

By heating such an alloy at 1700 degrees Cent. (3090 degrees Fahr.) for a few minutes and cooling rapidly, the structure is altered to that shown in Fig. 18 which is typical of such a peritectic reaction. Here the tungsten-rich solid solution (the solid zeta phase) has assumed the form of large rounded areas. Immediately adjoining these solid centers is the border of the intermetallic phase (light) while a network of residual cobalt-rich liquid (etched out) is left as far removed as possible from the tungsten-rich islands. By cooling more slowly through the range of temperature at which the reac-

tion may readily occur, the intermetallic phase is re-formed again quite completely resulting in the structure shown in Fig. 19.

As little as 2 per cent of cobalt is easily visible in the tungsten-rich matrix (Fig. 20) and when such a composition is heated above the peritectic temperature, it forms a broken network (Fig. 21), representing the liquid present above 1690 degrees Cent. Prolonged heating in the high temperature range, 1450 to 1650 degrees Cent. (2640 to 3000 degrees Fahr.) fails to completely dissolve 0.3 per cent cobalt (Fig. 22) but appears to result in a single phase when the cobalt content is reduced to 0.2 per cent.

The alloys last described containing less than 3 per cent tungsten were prepared by adding the cobalt as a standard solution of cobalt nitrate to the tungsten oxide. The resulting paste was thoroughly mixed, slowly dried and reduced in hydrogen. Analyses of the resulting metals showed the cobalt content to be within $\pm$ 0.03 per cent of the desired composition.

Cobalt will dissolve at the eutectic temperature 36 to 37 per cent of tungsten. As the temperature falls to 1100 degrees Cent. (2010 degrees Fahr.) the solid solubility of tungsten decreases along line FK (Fig. 1) to about 32 per cent. The diffusion rate is low, however, and to approximate a complete precipitation of the delta phase at 1150 degrees Cent. (2100 degrees Fahr.) requires from 25 to 50 hours. Figs. 24 and 25 show the elongated crystals of the delta phase precipitated from the cobalt-rich solid solution at 1125 degrees Cent. (2060 degrees Fahr.). Some delta from the eutectic is present at the grain boundaries in these fields. Again in Fig. 26 appear the delta crystals formed in a 35 per cent tungsten alloy during long heating at 1300 and 1150 degrees Cent. (2370 and 2100 degrees Fahr.).

Solid Solubility—Temperature Relations in the Cobalt-Rich Field

At a temperature between 1125 and 1075 degrees Cent. (2060 and 1970 degrees Fahr.) a reaction takes place between the delta phase and the cobalt-rich solid solution (beta phase) as indicated by the line KLMN in Fig. 1. This reaction takes place slowly and in its early stages results in structural features well illustrated in Figs. 27, 28, 29. In this alloy of 35 per cent tungsten the delta phase was precipitated in a rather massive form at the grain bounda-

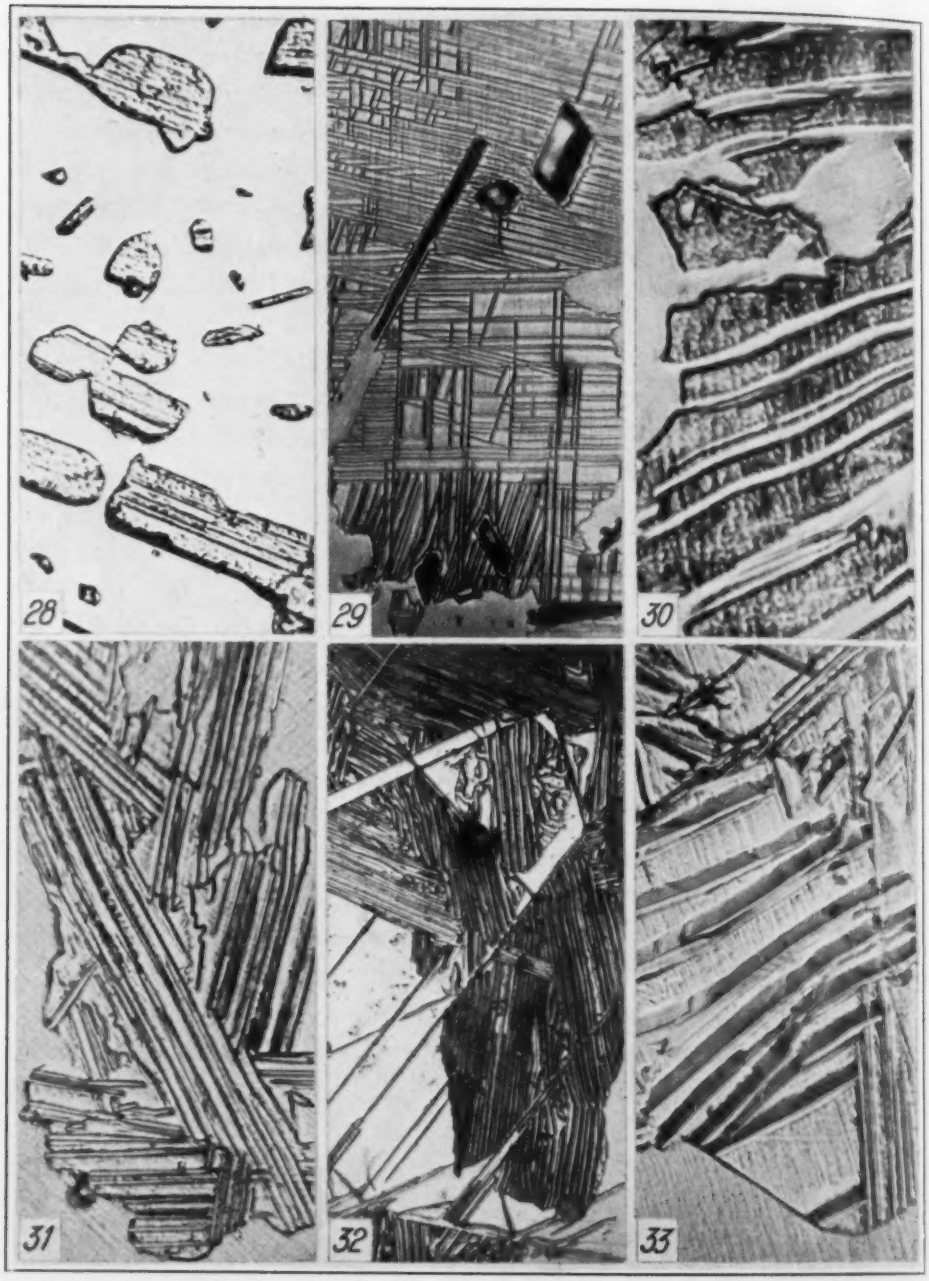


Fig. 28—Same Specimen as in Fig. 27 but Etched in Boiling Sodium Picrate for 15 Seconds. × 700.

Fig. 29—Cobalt plus 35 Per Cent Tungsten. Treated as Specimens in Figs. 27, 28. Then Heated at 1000 Degrees Cent. ± 15 Degrees Cent. for 50 Hours. Quenched. Etch (1) 10 Per Cent HCl plus H_2O_2. (2) Boiling Sodium Picrate. × 700.

Fig. 30—Detail of Epsilon Phase in Specimen Shown in Fig. 29. × 2000.

Fig. 31—Cobalt plus 30 Per Cent Tungsten. Melt Quenched from 1400 Degrees Cent. (2500 Degrees Fahr.) and Re-heated at 1050 ± 15 Degrees Cent. for 10 Hours. Quenched. Etched in 10 Per Cent HCl plus H_2O_2. × 1000.

Fig. 32—Cobalt plus 30 Per Cent Tungsten. Heated 1000 to 1025 Degrees Cent. for 25 Hours. 950 to 975 Degrees Cent. (1740 to 1790 Degrees Fahr.) for 25 Hours. Etched in 10 Per Cent HCl plus H_2O_2. × 500.

Fig. 33—Cobalt plus 30 Per Cent Tungsten. Showing Detail of Epsilon Precipitate, in Fig. 31. × 1000.

ries and in some scattered patches by a very slow cooling schedule from 1400 degrees Cent. (2550 degrees Fahr.) down to 1150 degrees Cent. (2100 degrees Fahr.). The identity of the delta phase at 1150 degrees Cent. is established by the sodium picrate etch as seen in Fig. 28.

After further heating at 1000 degrees Cent. for 50 hours (Fig. 29) the new epsilon phase has precipitated as a series of laminations or a latticework within the beta solid solution and also as massive borders about the pre-existing delta phase. A sodium picrate etch has dissolved the residual cores of the latter phase in the structure shown in Fig. 29. At a higher magnification (Fig. 30) the massive and the lamellar formations are seen to be continuous.

In the solid solution containing 30 per cent tungsten in which no excess delta exists the precipitation of the epsilon phase at temperatures slightly below 1100 degrees Cent. (2010 degrees Fahr.) occurs as shown in Figs. 31 and 32. This action usually begins at the grain boundaries and appears to progress outward in well-defined directions. In most cases a distinct boundary line seems to inclose the region in which the precipitation has occurred (Fig. 33). This might indicate the formation of a new form of crystal structure in the cobalt-rich solid solution, but, as will be noted later, the X-ray diffraction patterns do not show this to be the case. Due to the low rate of diffusion in these alloys the exact location of the temperature solubility line is somewhat difficult but an approximate determination is shown as the line KP in Fig. 23. Above 800 degrees Cent. (1470 degrees Fahr.) the existence of the epsilon phase could be positively detected in the microstructures of compositions to the right of the line KP. The location of the line at 800 degrees Cent. was determined by resistance measurements made upon alloy wires after suitable heat treatments to be described later.

Precipitation of the epsilon phase at temperatures below 1000 degrees Cent. may result in several interesting structural forms depending upon the tungsten concentration and the temperature. From solid solutions of intermediate tungsten content (i.e. 20 per cent) the precipitate which begins to separate at about 1000 degrees Cent. is still somewhat lamellar in appearance (See Fig. 34) but less closely packed than when formed from the more concentrated solutions.

At still lower tungsten concentrations and consequently lower temperatures of precipitation, the solid solution is first marked by

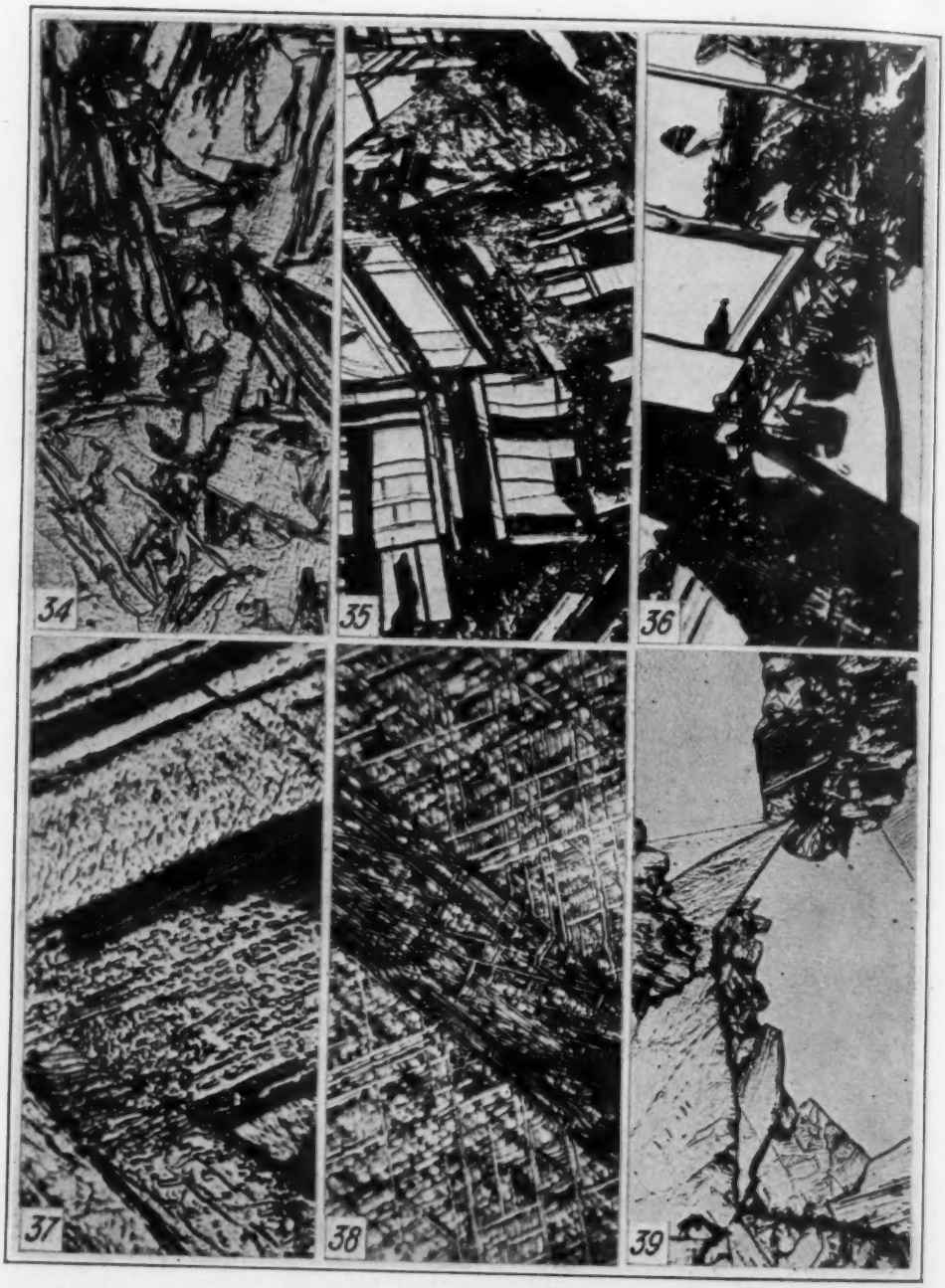


Fig. 34—Cobalt plus 20 Per Cent Tungsten. Melt, Rolled and Swaged. Re-heated at 1200 Degrees Cent. 50 Hours. Then 50 Hours at 900 Degrees Cent. Aqua Regia. × 500.

Fig. 35—Cobalt plus 10 Per Cent Tungsten. Melt Rolled and Swaged. Re-heated 25 Hours at 1200 Degrees Cent. Then at 800 ± 10 Degrees Cent. 50 Hours. Aqua Regia Etch. × 250.

Fig. 36—Cobalt plus 15 Per Cent Tungsten. Melt Rolled and Swaged. Re-heated 25 Hours at 1200 Degrees Cent. Then at 800 ± 10 Degrees Cent. for 25 Hours. Aqua Regia Etch. × 500.

Fig. 37—Cobalt plus 10 Per Cent Tungsten. Treatment Same as in Fig. 35 but Re-heated at 800 Degrees Cent. for 100 Hours. Aqua Regia Etch. × 1000.

Fig. 38—Cobalt plus 30 Per Cent Tungsten. Melt Quenched from 1450 Degrees Cent. Re-heated 900 ± 10 Degrees Cent. 15 Hours. × 1000.

Fig. 39—Cobalt plus 30 Per Cent Tungsten. Worked and Re-heated 1400 Degrees Cent. 25 Hours. Heated 5 Hours 700 Degrees Cent. 10% HCl-H_2O_2. × 200.

darkened blocks of a general rectangular outline (Fig. 35). A certain amount of closely spaced lamellar structure often appears under these conditions usually outlining the original grains of solid solution as in Fig. 36.

With prolonged heating the darkened bands mentioned above resolve into lines of elongated globules easily visible at 1000 diameters and shown in Fig. 37. In the solid solutions of higher tungsten concentration precipitation occurring in the temperature range of 1000 to 800 degrees Cent. (1830 to 1525 degrees Fahr.) results in the "cross hatched" appearance of which the microstructure in Fig. 38 is typical.

At 700 degrees Cent. (1290 degrees Fahr.) and below, however, the change in structure begins at the grain boundaries as shown in Figs. 39 and 40. Such areas, which darken rapidly upon etching suggest the formation of new structural units in the solid solution growing somewhat radially from the line or center of origin. Isolated formations of this type often develop at some distance from a grain boundary (Fig. 41).

This formation spreads throughout the entire section if the heating is continued for perhaps 200 hours at 600 to 650 degrees Cent. (1110 to 1200 degrees Fahr.). The entire section in such a case has the appearance of the field in Fig. 42 and as will be noted later this condition is representative of the alloy in its hardest state.

The Epsilon Phase

Alloys formed by prolonged sintering of the pressed metal powders were found most suitable for approximating the composition range of the epsilon phase. This method of preparation eliminates the possibility of tungsten-rich segregations due to widely differing densities of the constituents. A fairly uniform and intimate mixture of the cobalt-rich solid solution and the delta phase could be produced by this method when metals were sintered for 75 or 100 hours at 1425 to 1450 degrees Cent. (2600 to 2640 degrees Fahr.). After thus forming the alloys a series of specimens were heated at 1050 $\pm$ 15 degrees Cent. (1920 degrees Fahr.) for various periods of time up to 100 hours to note the progress in the formation of the epsilon phase.

Compositions between 45 and 51 per cent tungsten were treated in this manner. While the single phase was in no case completely

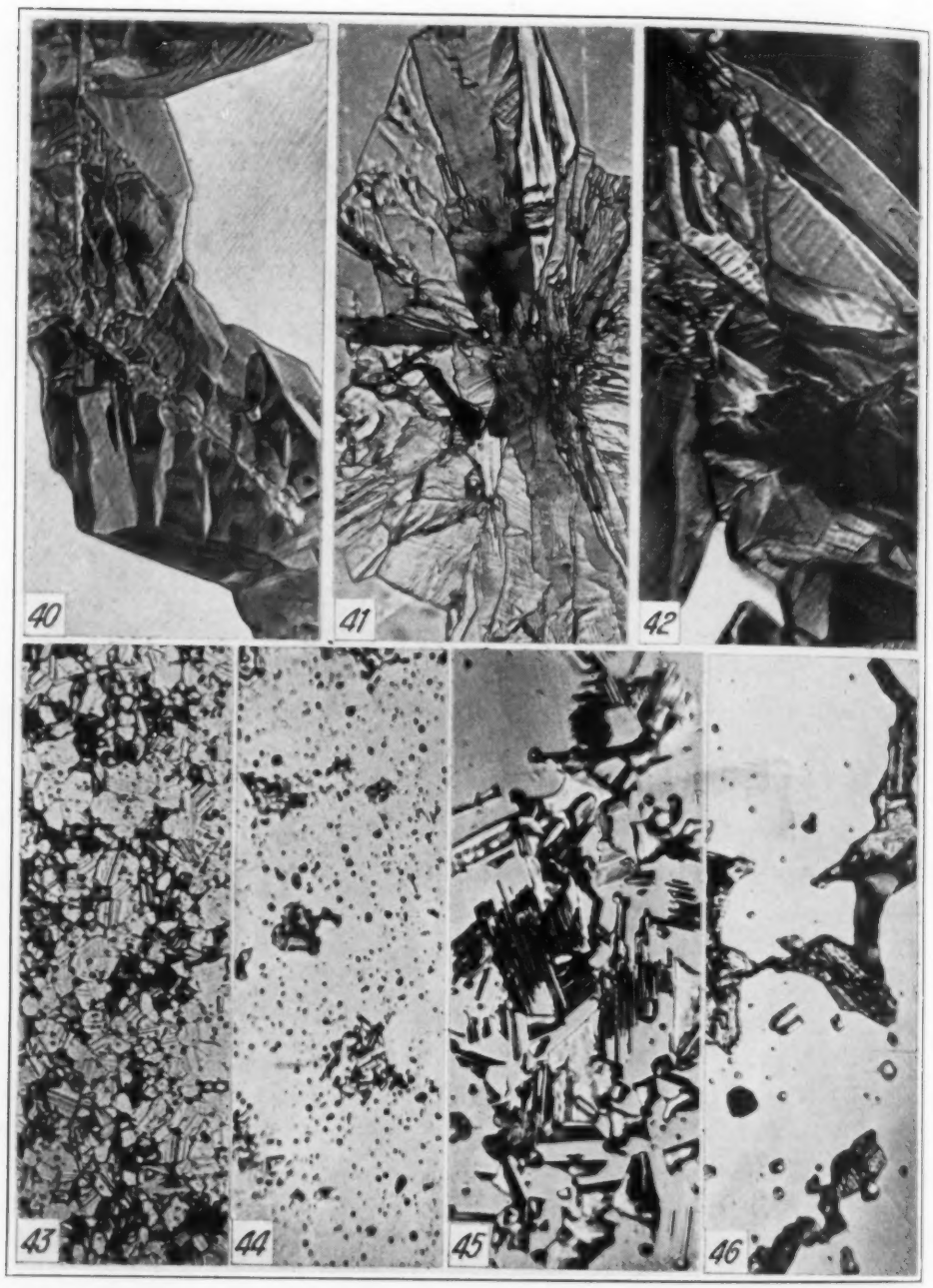


Fig. 40—Cobalt plus 30 Per Cent Tungsten. Worked and Re-heated at 1400 Degrees Cent. 25 Hours. Heated 600 Degrees Cent. 25 Hours. 10 Per Cent HCl plus H_2O_2. × 1000.

Fig. 41—Same as Fig. 40 After Heating at 600 Degrees Cent. 100 Hours. × 500.

Fig. 42—Same Specimen Shown in Fig. 41. Etched in Aqua Regia. × 1000.

Fig. 43—Cobalt 53 Per Cent, Tungsten 47 Per Cent. Sintered at 1450 Degrees Cent. 100 Hours. Etched in (1) 10 Per Cent HCl plus H_2O_2. (2) Boiling Sodium Picrate. × 250.

Fig. 44—Same as Fig. 43, with Additional Heating at 1050 ± 15 Degrees Cent. 100 Hours. Etch (1) 10 Per Cent HCl plus H_2O_2. (2) Boiling Sodium Picrate. × 250.

Fig. 45—Detail of Residual Cobalt-rich Area in Specimen Shown in Fig. 44. Etched in 10 Per Cent HCl plus H_2O_2. × 1000.

Fig. 46—Detail of Residual Area of the Delta Phase in Same Specimen. Etched in Boiling Sodium Picrate. × 1000.

formed, the resulting microstructure indicated a narrow range of composition for this phase. The composition may extend from 45 to 47 per cent tungsten but certainly is of no wider range. The structure shown in Fig. 43 is that of the 47 per cent tungsten alloy as sintered 75 hours at 1425 to 1450 degrees Cent. (2600 to 2640 degrees Fahr.). In the lighter cobalt-rich phase the characteristic twinning bands can be seen. A sodium picrate etch had darkened the scattered areas of the delta phase.

After heating at 1050 ± 15 degrees Cent. (1920 degrees Fahr.) for 75 hours the reaction has so far progressed as to leave only a few scattered spots of the two original phases (Fig. 44). The small round black spots scattered throughout the field are cavities which always occur in alloys formed by sintering. Near the center and left side of the field are seen two dark areas of irregular outline which represent residual delta, colored by the sodium picrate etch. Below these spots to the left and right, appear two of the cobalt-rich phase. The banded arrangement of the first epsilon precipitate is still to be seen in these latter areas (Fig. 45), especially at higher magnifications. In Fig. 46 is shown a small area of the residual delta phase surrounded by the solid field of epsilon.

Since the remaining sources of cobalt and tungsten necessary to complete the reaction are at this stage so remotely separated it is improbable that the reaction could be brought to completion in any reasonable length of time.

While the evidence furnished by the microstructure is not conclusive it indicates that the composition limit of the epsilon phase on the tungsten-rich side lies at about 47 per cent tungsten. This corresponds closely with the theoretical composition of intermetallic compound Co_7W_2 (47.1 per cent tungsten).

In compositions richer in tungsten than 70 per cent no changes below 1650 degrees Cent. (3000 degrees Fahr.) were indicated either by the microstructures or the diffraction patterns.

X-Ray Diffraction Patterns

In Fig. 47 are shown the characteristic patterns of pure cobalt made from specimens of the hydrogen-reduced powder. The upper pattern (47-A) represents the face-centered cubic form produced by hydrogen reduction of the oxide at a temperature of 900 degrees Cent. (1650 degrees Fahr.) and cooled in hydrogen to room tem-

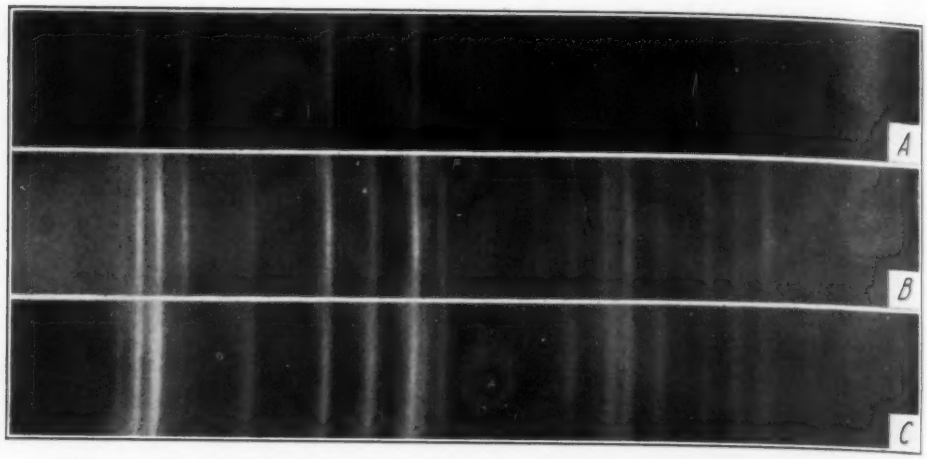


Fig. 47-A—Cobalt Metal Powder Reduced at 950 Degrees Cent. (1740 Degrees Fahr.) for 12 Hours.

Fig. 47-B—Cobalt Metal Powder Reduced at 950 Degrees Cent. (1740 Degrees Fahr.) and Re-heated at 1200 Degrees Cent. (2190 Degrees Fahr.) for 15 Hours.

Fig. 47-C—Cobalt Metal Powder (Part of Specimen 47-A) Hammered at Room Temperature.

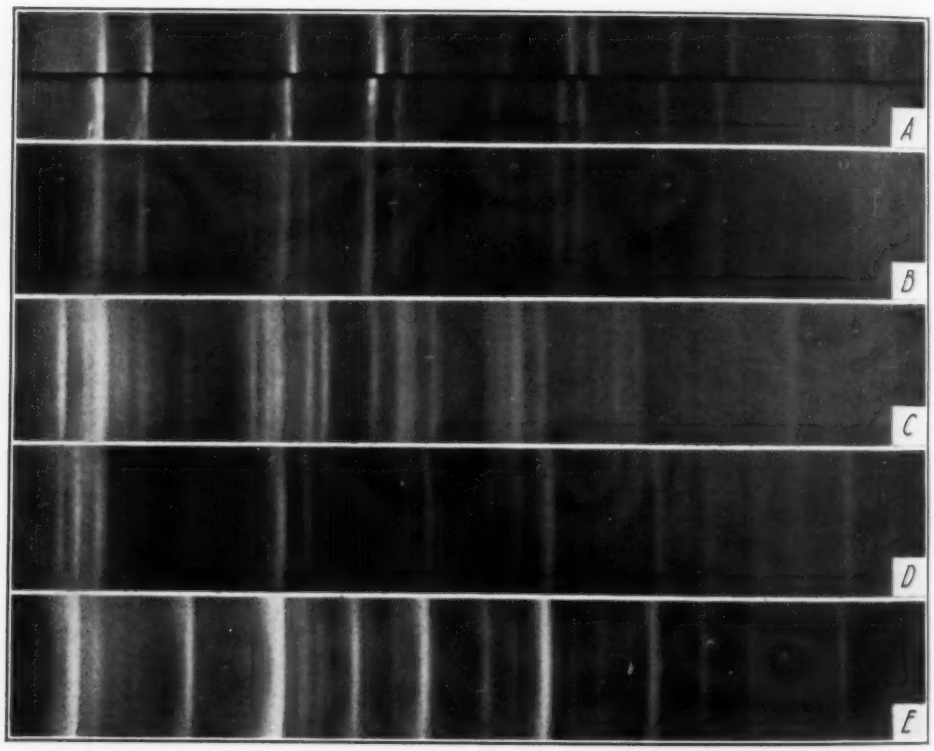


Fig. 48-A—Upper Cobalt Metal Powder Reduced at 950 Degrees Cent. (1740 Degrees Fahr.). Lower—Cobalt plus 35 Per Cent Tungsten, Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours.

Fig. 48-B—Cobalt, 50 Per Cent, Tungsten, 50 Per Cent, Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours.

Fig. 48-C—Tungsten, 68 Per Cent, Cobalt, 32 Per Cent. Formed as 48-B.

Fig. 48-D—Tungsten, 80 Per Cent, Cobalt, 20 Per Cent. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 25 Hours. 1550 to 1600 Degrees Cent. (2820 to 2910 Degrees Fahr.) for 25 Hours.

Fig. 48-E—Tungsten, 90 Per Cent, Cobalt, 10 Per Cent. Sintered as 48-D.

perature. A second part of this same specimen was subsequently heated at 1200 degrees Cent. (2190 degrees Fahr.) in hydrogen for several hours. This pattern (47-B) contains the lines of both the face-centered cubic and the hexagonal close-packed lattices. By hammering a third portion of the original metal powder, a pattern results (47-C) which is almost exclusively that of the hexagonal form.

Solid solutions of tungsten in cobalt made by sintering the pressed powders at 1400 to 1450 degrees Cent. (2550 to 2640 degrees Fahr.) for 50 hours yield the pure face-centered cubic pattern only when the tungsten composition exceeds about 30 per cent. Alloys formed in this manner are especially suitable for diffraction patterns because of their relatively small grain size. The alloys made by melting result in spotty patterns. It was found possible to produce the solid solutions of cobalt containing 10 per cent and 20 per cent tungsten by mixing the oxides and reducing the mixture at 1050 degrees Cent. (1920 degrees Fahr.), thus eliminating the pressing operation. The patterns from metal so treated proved to be those of the pure face-centered cubic form. By re-heating portions of such specimens to successively higher temperatures the approximate location of the line QD in the constitutional diagram (Fig. 1) was confirmed.

By the addition of 35 per cent tungsten to cobalt the field of the face-centered cubic form appears to be extended upwards to the temperature of the solidus. The parameter of the face-centered cubic lattice is expanded as shown in Fig. 48-A in which the patterns of cobalt and that of the 35 per cent tungsten solid solution were recorded by one exposure on the same film. Approximate measurements of the patterns from three separate specimens of this composition resulted in a value of 3.581 $\pm$ 0.006 Å for the edge of the elementary cube. This represents an increase of about 1.9 per cent over the corresponding dimension (3.512 Å) in the lattice of pure cobalt.

The diffraction patterns obtained from compositions between 30 and 90 per cent tungsten and treated at temperatures above 1100 degrees Cent. (2010 degrees Fahr.) are shown in Fig. 48.

Lines of the delta pattern become visible when the tungsten content exceeds some 40 per cent. In Fig. 48-B this pattern occurs along with that of the cobalt-rich solid solution.

In Fig. 48-C is shown the most completely developed pattern observed as representative of the delta phase. The lines of the

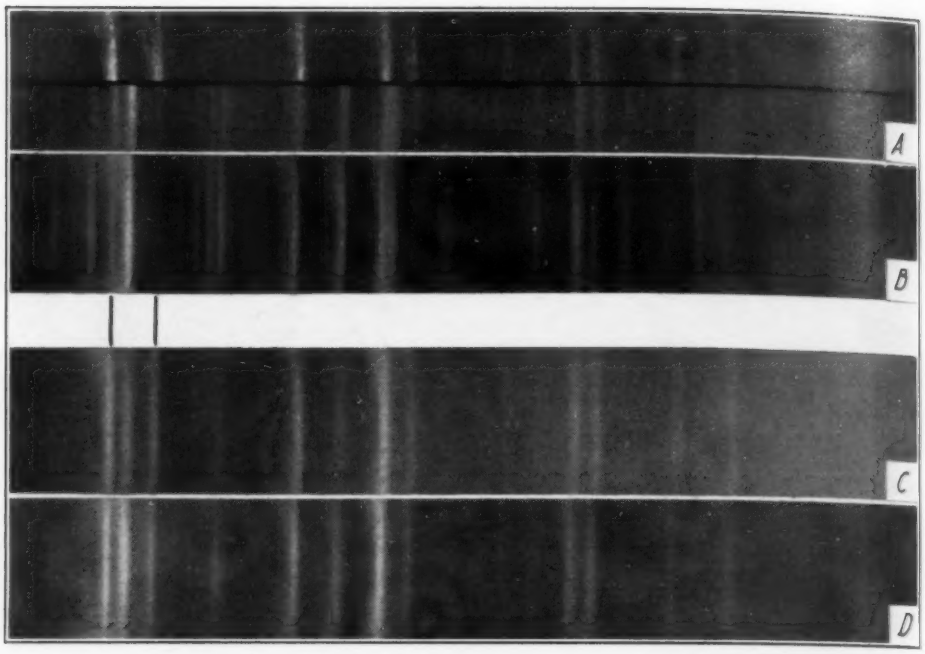


Fig. 49-A—Upper—Cobalt, 65 Per Cent. Tungsten, 35 Per Cent. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours. Lower—Cobalt, 58 Per Cent, Tungsten, 42 Per Cent. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours. Re-heated 1050 ± 10 Degrees Cent. (1920 Degrees Fahr.) for 50 Hours.

Fig. 49-B—Cobalt, 50 Per Cent, Tungsten, 50 Per Cent. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours. Re-heated 1050 ± 10 Degrees Cent. (1920 Degrees Fahr.) for 150 Hours.

Fig. 49-C—Cobalt, 70 Per Cent, Tungsten, 30 Per Cent. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours. Re-heated 1025 ± 15 Degrees Cent. (1875 Degrees Fahr.) for 5 Hours. Two Lines of Cobalt-rich Solution Indicated Above this Pattern.

Fig. 49-D—Same as 49-C. Re-heated 1025 ± 15 Degrees Cent. for 50 Hours.

tungsten pattern are easily visible in next pattern (48-D) and become prominent in the pattern from the 90 per cent tungsten alloy (48-E).

Below 1100 degrees Cent. (2010 degrees Fahr.) the epsilon phase exists together with the cobalt-rich solid solution in the range of composition between approximately 3 and 45 per cent tungsten.

Its pattern is seen in the lower half of Fig. 49-A as formed in a 42 per cent tungsten alloy at 1050 degrees Cent. (1920 degrees Fahr.). At this temperature the concentration of tungsten in the cobalt-rich solid solution has decreased to about 25 per cent. The resulting change in parameter of the solid solution lattice is visible in the lower pattern of this figure.

A well-developed pattern of the epsilon phase is shown in Fig. 49-B. In the following patterns (Fig. 49-C, D) several lines of the epsilon phase appear along with those of the face-centered cubic

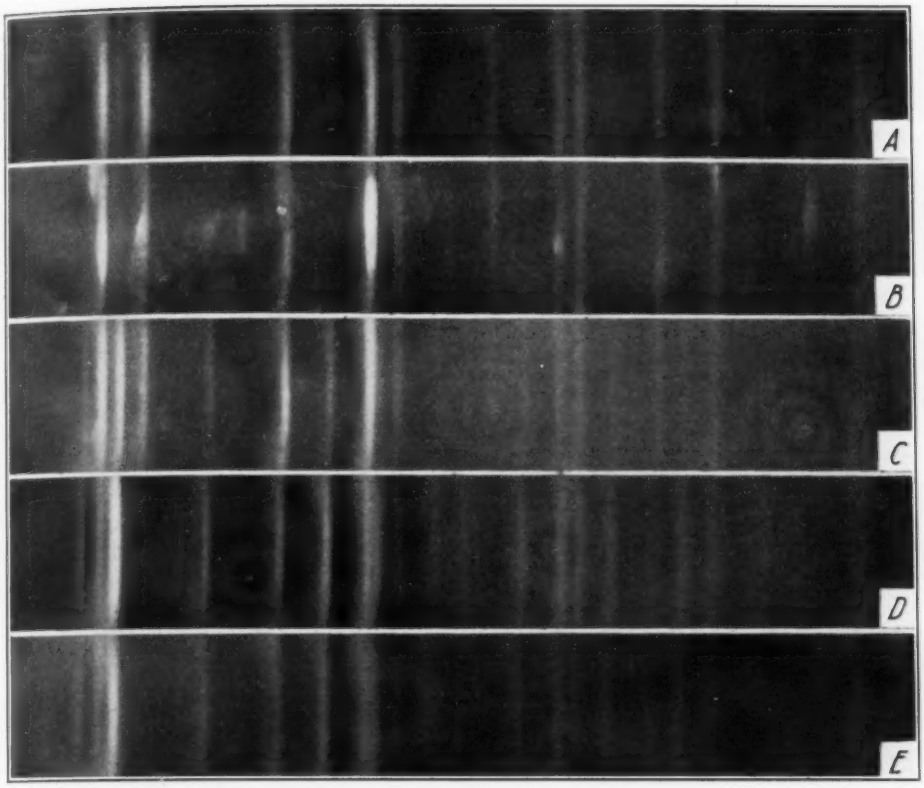


Fig. 50-A—Cobalt plus 30 Per Cent Tungsten. Sintered 1425 to 1450 Degrees Cent. (2600 to 2640 Degrees Fahr.) for 50 Hours. Rockwell C32.
Fig. 50-B—Same. Aged 600 Degrees Cent. (1110 Degrees Fahr.) for 1 Hour. C-35.
Fig. 50-C—Same. Aged 600 Degrees Cent. (1110 Degrees Fahr.) for 5 Hours. C-39.
Fig. 50-D—Same. Aged 600 Degrees Cent. (1110 Degrees Fahr.) for 25 Hours. C-59.
Fig. 50-E—Same. Aged 600 Degrees Cent. (1110 Degrees Fahr.) for 100 Hours. C-62.

cobalt-rich solid solution. This specimen after its preliminary treatment at 1425 degrees Cent. (2600 degrees Fahr.) was heated at 1000-1025 degrees Cent. (1830-1880 degrees Fahr.) for 50 hours. The epsilon phase will appear in the microstructure as the lamellar formation seen in Fig. 32.

If the precipitation of the epsilon phase is carried on at a lower temperature (i.e., 600 to 700 degrees Cent.) by prolonged heating, the relatively large quantity of precipitated epsilon results in a pattern of this phase (Fig. 50-D). This is increasingly noticeable in compositions richer than 15 per cent in tungsten.

Age hardening at 600 degrees Cent. (1110 degrees Fahr.) in a 30 per cent tungsten alloy is accompanied by the changes in diffraction pattern seen in the series of Fig. 50.

The first pattern (A) is that of the sintered alloy having a Rockwell hardness number of C 32. A few lines of the hexagonal form

persist in this specimen despite the 50 hours of sintering at 1400 to 1450 degrees Cent. (2640 degrees Fahr.).

After aging for 1 hour at 600 degrees Cent. with a resulting rise in hardness to C 35, the pattern assumes a decidedly "spotty" appearance. The lines appear to be less diffuse and a scattering of reflected target images occurs over a considerable length of the pattern. After heating at 600 degrees Cent. for 5 hours some full lines of the epsilon phase have developed and the "spotty" reflections have greatly diminished both in number and in intensity. Of the original pattern at least the second and third lines appear to have maintained their position.

At the end of 25 hours the reflections of the normal epsilon pattern appear to be well-developed though this is as yet incomplete. Note that in this pattern the second of the face-centered cubic lines is entirely absent. The last pattern (50-E) is that from a specimen aged at 600 degrees Cent. for 100 hours and represents the alloy at about maximum hardness. The pattern is now fairly complete as will be obvious by comparison with that in Fig. 49-B.

The computed interplanar spacings from the patterns of the delta and epsilon phases were compared with the plots of Hull and Davey in an attempt to determine the crystal lattices of these phases. In the case of the delta phase the first ten lines matched almost exactly the theoretical positions demanded by a simple triangular lattice with an axial ratio of 1.40. Three reflections between the tenth and sixteenth spacings on the chart are barely visible in the pattern.

The interplanar spacings from the epsilon pattern correspond closely with those plotted for the face-centered tetragonal lattice with an axial ratio between 1.32 and 1.28. In this case, two reflections fail to appear between the spacings 1.47 Å and 1.20 Å, corresponding to the tenth and eleventh lines in the pattern.

While these data are not sufficiently complete to identify with certainty the lattice types, it is included for purposes of comparison with more exact determinations which may possibly be made at some future time.

Hardness Characteristics

The hardness of the cobalt-rich solid solutions rises continuously with the addition of tungsten up to the limit of saturation at about 38 per cent tungsten.

As indicated by the lower curve in Fig. 51 the first additions

of tungsten appear to be somewhat more effective in hardening than is the case after the tungsten content has exceeded 15 or 20 per cent.

It is possible that this effect is connected with the allotropic changes which must occur to some extent in these compositions,

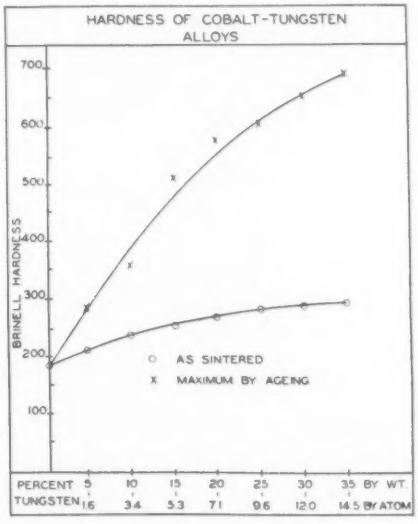


Fig. 51—Diagram Showing Hardening Versus Tungsten Content.

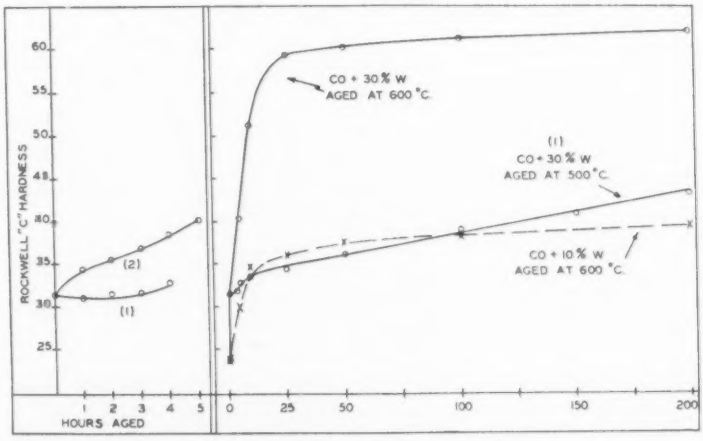


Fig. 52—Diagram Showing Age-hardening.

when cooled from 1400 degrees Cent. (2550 degrees Fahr.). Due to the slow rate of diffusion in these solid solutions it is unnecessary to quench from the elevated temperatures (1400-1450 degrees Cent.) in order to maintain the supersaturated state.

Upon re-heating at a temperature of 500 degrees Cent. a slow but continuous increase in hardness sets in (Fig. 52). This hard-

ness increase, accompanying the precipitation of the epsilon phase, goes on more rapidly at higher aging temperatures. After heating at 550 degrees Cent. (1020 degrees Fahr.) for 400 hours hardness of a 35 per cent tungsten alloy has increased from Rockwell C 33 to C 63. The Brinell numbers of this alloy in the corresponding con-

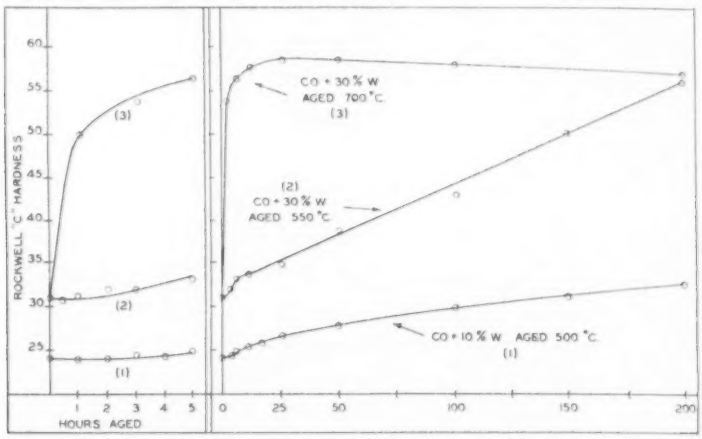


Fig. 53—Diagram Showing Age-hardening.

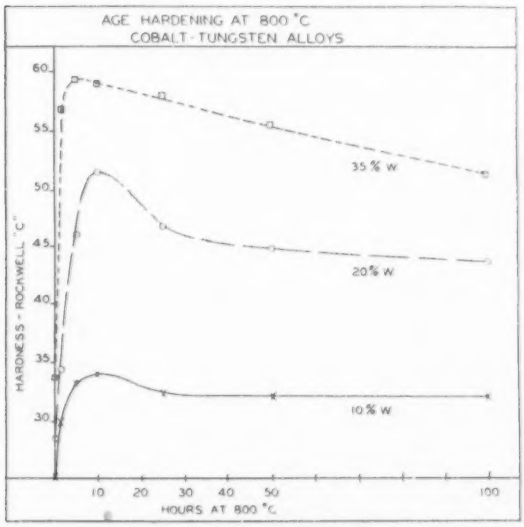


Fig. 54—Diagram Showing Age-hardening.

ditions were 295 and 690. This hardness is the maximum observed in any of the solid-solution alloys prepared by pressing and sintering.

A somewhat higher hardness was developed by a 35 per cent tungsten alloy prepared by melting and subsequently rolled. This, after aging at 600 degrees Cent. for 200 hours in the rolled condition.

Table I

Hardness of Cobalt-Tungsten Alloys Sintered 1400-1450 Degrees Cent. (2550-2640 Degrees Fahr.)—2 Hours

Composition	Hardness as Quenched		Maximum Hardness by Aging	
	Rockwell C	Brinell	Rockwell C	Brinell
Cobalt	8	185	....	...
Co + 5% W	20	210	29	280
10% W	23.5	240	38.5	355
15% W	26.0	255	54.5	515
20% W	27.5	270	58.0	585
25% W	29.0	280	59.0	600
30% W	31.5	285	61.5	630
35% W	33.5	295	63.0	690

Table II

Age-Hardening in Alloy of Cobalt + 35 Per Cent Tungsten

Aging Time Hours	Temperature 550° C.		Temperature 600° C.		Temperature 700° C.		Temperature 800° C.	
	Rockwell C	Brinell	Rockwell C	Brinell	Rockwell C	Brinell	Rockwell C	Brinell
1	....	...	....	...	50	480	53	500
5	36.5	330	42.5	370	56	545	58	580
10	38	...	54.5	515	57	560	57	560
25	39.5	350	60.0	615	58	585	55	530
50	47.5	...	61.0	620	59	600	54.5	515
100	53.5	490	61.5	630	59	600	51	470
200	61	620	62.0	645	59	600	..	...
300	62.5	660	....	...	..	...	..	...
400	63	690	....	...	..	...	..	...

As-sintered 1400-1450 degrees Cent. (2550-2640 degrees Fahr.)—2 Hours.
Rockwell C 33.5.
Brinell 295.

Table III

Age-Hardening in Alloy of Cobalt + 35 Per Cent Tungsten Rolled at 800 to 1000 Degrees Cent. (1470 to 1830 Degrees Fahr.)—75 Per Cent Reduction

Aging Time Hours	Temperature 600° C.		Temperature 700° C.		Temperature 800° C.	
	Rockwell C	Brinell	Rockwell C	Brinell	Rockwell C	Brinell
1	..	...	60	610	61	655
5	48	415	62	670	62	675
10	58	585	63	690	63	685
25	62	635	64	720	60	610
50	64	720	64	730	55	530
100	65	770	65	770	..	...
200	65	770	64	710	..	...

Hardness as-rolled.
Rockwell C 39.
Brinell 330.
This alloy prepared by melting in a hydrogen atmosphere.

increased in hardness from C 39 to C 65. Brinell 330 to 770. The aging characteristics of the alloys in general are listed in Tables I, II and III.

No positive softening during the first stages of aging could be detected although at 500 and 550 degrees Cent. the hardness remains unchanged for the first two or three hours. In some specimens a decrease in hardness of a full point on the Rockwell "C" scale was observed after the first hour at 550 degrees Cent. In others, of the same composition, however, this did not occur. The data used in constructing the curves in Figs. 52, 53, and 54, are the average of four readings on each of six specimens. With the use of material of more nearly uniform hardness and a sufficiently large number of specimens the detection of a positive decrease in hardness during the early stages of aging might be possible.

As compared to the corresponding solid solutions of the iron-tungsten alloys those in the cobalt-tungsten system develop a maximum secondary hardness higher by some 50 per cent. While age-hardening begins at about 100 degrees Cent. lower in the cobalt-tungsten system than in the iron-tungsten, the hardness of the latter appears to be less persistent at temperatures of 700 and 800 degrees Cent.

Resistance Measurements

For the purpose of determining the solid solubility of tungsten in cobalt at temperatures between 800 and 550 degrees Cent. measurements of electrical resistance were made on a series of wires. The wires as noted previously were made from the hydrogen-melted metals, by hot rolling, swaging, and drawing to a finished diameter which varied among the several lengths between 0.0250 and 0.0251 inch.

To insure the formation of the single-phase solid solution the wires in 6-inch lengths were heated at 1150 to 1200 degrees Cent. (2100 to 2190 degrees Fahr.) for 15 hours in hydrogen and cooled quickly in hydrogen to room temperature. During this heating the wires were packed in silica tubes and consequently were relatively straight when removed from the furnace.

Three specimens of each composition were used in all the measurements undertaken, each individual having a distinctive marking so that the resistance of any particular wire could be followed throughout subsequent heat treatments.

The wire as mounted for measurements was held straight in grooved supports by bakelite clamps and the currrent contacts made at either end through metal clips. The potential leads were taken

from two metal V-shaped knife edges which were fixed in a bakelite rider set upon the wire specimen. In series with the specimen was a variable resistance and also a standard fixed resistance unit of 0.1 ohm. A current of about 0.1 ampere was supplied from a source of nearly constant voltage. By means of a galvanometer and Type K potentiometer, the potential drops across the standard resistance and across the wire between the knife edges were measured alternately to 0.01 millivolt. Three separate readings on the standard and two on

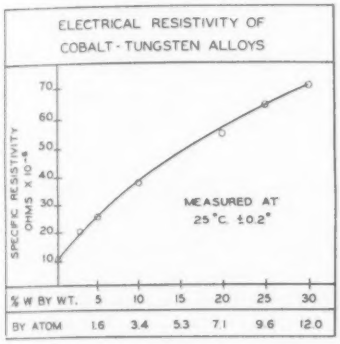


Fig. 55—Diagram Showing Specific Resistivity Versus Tungsten Content.

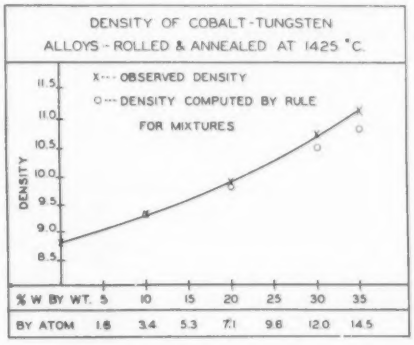


Fig. 56—Diagram Showing Density Versus Tungsten Content.

the specimen were taken at each setting. The wire in its mounting was immersed in a kerosene bath, kept at a temperature of 25 ± 0.2 degrees Cent.

A value of 10.5 (± 0.1) x 10^{-6} ohms was obtained for the specific resistivity of the cobalt. This is an average from measurements upon twelve specimens. According to the work of Kalmus and Harper[6] the specific resistivity of pure cobalt at 18 degrees Cent. is 8.964 x 10^{-6} while the value of 9.7 x 10^{-6} appears in the International Critical Tables. The impurities (about 1 per cent) known to be present in the cobalt used in this work no doubt account for the higher value obtained for the specific resistivity.

The relation between tungsten content and specific resistivity is shown by the curve in Fig. 55, while the resistivity values of the series of compositions are listed in Table IV.

A series of wires from the alloys containing 3, 5, and 10 per cent tungsten after annealing at 1150-1200 degrees Cent. (2100-2190 degrees Fahr.) and rapidly cooling were used to locate the limits of the solid solution field below 800 degrees Cent. (1470 degrees Fahr.) (Line KP in Fig. 23).

Table IV
Specific Electrical Resistivity at 25 ± 0.2 Degrees Cent.
Diameter of Wire = 0.02505 ± 0.00005 Inch
Measured Length = 3.990 Inch

Specific Resistivity ± 0.1 Ohms x 10^{-6}	Composition
10.5	Cobalt
20.1	Cobalt + 3% W
25.5	Cobalt + 5% W
37.6	Cobalt + 10% W
54.0	Cobalt + 20% W
62.9	Cobalt + 25% W
70.1	Cobalt + 30% W

Wires annealed 1400 degrees Cent. (2550 degrees Fahr.) for 15 hours and cooled quickly to room temperature.

Table V
Resistance in Ohms of Wires After Re-Heating in Hydrogen for 100 Hours at Designated Temperature Measured at 25 ± 0.2 Degrees Cent.

		As Annealed	Reheated 100 Hours at			
Composition	Mark	1150-1200 Degrees Cent. (2100-2190 Degrees Fahr.)	800 ± 10 Degrees Cent. (1470 Degrees Fahr.)	700 ± 10 Degrees Cent. (1290 Degrees Fahr.)	600 ± 10 Degrees Cent. (1110 Degrees Fahr.)	550 ± 10 Degrees Cent. (1020 Degrees Fahr.)
Cobalt	Co-67-1	0.0334	0.0336	0.0336	0.0336	0.0334
	2	0.0346	0.0348	0.0348	0.0346	0.0346
	3	0.0348	0.0347	0.0349	0.0348	0.0347
	Avg.	0.0343	0.0344	0.0344	0.0343	0.0342
Co + 3% W	W-Co-50-1	0.0662	0.0661	0.0659	0.0664	0.0658
	2	0.0652	0.0650	0.0649	0.0651	0.0649
	3	0.0664	0.0662	0.0664	0.0665	0.0663
	Avg.	0.0659	0.0658	0.0660	0.0660	0.0657
Co + 5% W	W-Co-65-1	0.0820	0.0821	0.0820	0.0744	0.0717
	2	0.0819	0.0821	0.0820	0.0735	0.0709
	3	0.0821	0.0823	0.0822	0.0746	0.0720
	Avg.	0.0820	0.0822	0.0821	0.0742	0.0715
Co + 10% W	W-Co-66-1	0.1209	0.0865	0.0710	0.0648	
	2	0.1216	0.0865	0.0705	0.0645	
	3	0.1206	0.0865	0.0704	0.0643	
	Avg.	0.1210	0.0865	0.0706	0.0645	

Three specimens of each composition along with wires of cobalt for a control were heated for 100 hours at 800 degrees Cent. (1470 degrees Fahr.) in a hydrogen atmosphere and cooled quickly to room temperature. The resistance was then measured as described above. As may be noted on the first columns of Table V, the resistance of the 10 per cent tungsten alloy has decreased during this treatment by some 30 per cent. The other compositions show no changes exceeding ± 0.0003 ohms which figure represents the degree of ac-

curacy expected from these measurements. From this fall in resistance it may be concluded that the composition in question lies at 800 degrees Cent. in the two-phase field.

Subsequent heatings at 700, 600 and 550 degrees Cent. result in a change in the 5 per cent tungsten specimen but have no measurable effect upon the resistance of the wire containing 3 per cent tungsten.

Density Determinations

Density determinations were made upon several specimens of cobalt metal, as-cast, as-rolled, and as-rolled and annealed. The metal was melted in hydrogen and each specimen used for the density measurements weighed about 25 grams. The weight in air was determined to ± 0.0001 gram, and in distilled water (at 25 ± 0.3 degrees Cent.) the weight could be measured with an accuracy of ± 0.0003 gram.

Table VI
Density of Cobalt Metal Expressed in Terms of Density of Water at 4 Degrees Centigrade

Specimen	Density	Average
A	8.811	
B	8.816	8.813
C	8.835	
D	8.836	
E	8.827	8.833

History of Specimens

A and B—From separate lots of metal as melted and solidified in a hydrogen atmosphere.
C—Metal prepared as "A" and "B" then rolled at about 1000 degrees Cent. to 75 per cent reduction in cross-sectional area.
D—Treated as "C" and annealed 1100 to 1200 degrees Cent. (2010 to 2190 degrees Fahr.) for 15 hours.
E—Annealed 1400 to 1425 degrees Cent. (2550 to 2600 degrees Fahr.) for 15 hours.

The resulting values (8.81-8.83) are listed in Table VI. These seem to be in fair agreement with the value of 8.97 calculated from the X-ray data as noted previously. (See page 407.) Kalmus and Harper report the density of pure cobalt as annealed, 8.810 and as swaged 8.925.

The measured densities of a series of cobalt-rich solid solutions containing up to 35 per cent by weight of tungsten are listed in Table VII. In the second column of this table are the density values computed by the rule of mixtures. The density is plotted against tungsten content in Fig. 56. The observed density becomes increasingly

Table VII

Densities of Cobalt-Tungsten Alloys Expressed in Terms of Density of Water at 4 Degrees Cent.

Composition	Density (Observed)	Density Computed by Rule for Mixtures (Density of Co = 8.83) (Density of W = 19.3)	Computed from X-Ray Diffraction Data
Cobalt	8.83	.....	8.97
Co + 10% W	9.34	9.34	.....
Co + 20% W	9.98	9.90	.....
Co + 30% W	10.71	10.52	.....
Co + 35% W	11.11	10.89	11.14

Alloys made by melting in hydrogen, rolling to 75 per cent reduction in cross-section, annealing at 1400-1425 degrees Cent. (2550 to 2600 degrees Fahr.) for 15 hours and quenching in water.

greater than the calculated density as the tungsten content rises above 10 per cent by weight. This difference amounts to some 2 per cent in the solid solution containing 35 per cent tungsten which concentration is near the saturation limit of the solid solution. Using the value 3.581 Å for the edge of the elementary cube the density computations on the basis of replacement for the 35 per cent tungsten solid solution result in the figure 11.14. As listed in Table VI the density of this composition as determined by the method of weighings is 11.11.

Practical Considerations

Cobalt-tungsten alloys ranging in composition from 20 to 35 per cent tungsten have been in use for some time as swaging dies for the hot working of tungsten metal.

These dies are prepared by pressing the mixed powders and sintering for two hours at 1400 to 1450 degrees Cent. (2550 to 2640 degrees Fahr.). After the sintering operation the alloy blocks are machined to the desired shape and dimension and then aged at 650 degrees Cent. for about 50 hours.

Any of the compositions within the range from 20 to 35 per cent tungsten resist wear in the tungsten swaging operations much better than any alloys previously used for this purpose. The composition 80 per cent cobalt, 20 per cent tungsten appears to be the most satisfactory. This alloy does not exhibit the tendency to chip in service which is shown to some extent by the compositions of 30 and 35 per cent tungsten.

Although the hardness of the 20 per cent alloy after aging is but C 50 to 52, the dies will hold their original size over months of con-

tinuous use. The only change in dimension observed is a slight decrease in diameter of bearing which is remedied by relapping to size. In view of the elevated temperatures 1200 to 1500 degrees Cent. (2190 to 2730 degrees Fahr.) of the tungsten metal upon which these dies work, the alloys appear to possess remarkable resistance to deformation at high temperatures.

Acknowledgments

Some of the age hardening characteristics of the cobalt-rich solid solutions of tungsten were studied by Howard L. Hopkins[10] in 1930 at the Cleveland Wire Works under the guidance of the present author. His data was submitted as a thesis to Case School of Applied Science for a B. S. degree in Metallurgical Engineering.

The resistance measurements reported in this paper were obtained with the assistance of A. B. Gladding of the Cleveland Wire Works. The author is indebted to Mr. Gladding, in addition, for the many X-ray diffraction patterns made in connection with this investigation.

DISCUSSION

Written Discussion: By Robert F. Mehl, Director Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh.

It might here be recorded that G. Wassermann has recently studied the solid-solid transitions in cobalt (*Metallwirtschaft,* Vol. 11, 1932, pp. 61-65). It was found that cold-rolled cobalt was hexagonal in structure, possessing a preferred orientation similar to that of cold-rolled zinc and cadmium. This fiber-structure was retained on heating to 450 degrees Cent. At higher temperatures, however, a cubic structure (beta) quickly appeared, a structure retained both on quenching or slow cooling to room temperature. To transform this unstable structure to the stable hexagonal (alpha) structure it was found necessary to cold-roll. The temperature of the alpha-beta transition was accordingly found to be somewhat above 450 degrees Cent. To establish this temperature more accurately Wassermann made dilatometric measurements during the heating of cold-rolled sheet; these measurements showed a discontinuity between 400 and 480 degrees Cent. badly spread, probably because of superimposed effects originating in the cold work. In any event, the alpha-beta transformation may be taken to be about 450 degrees Cent.

Cobalt rolled between 450 and 1015 degrees Cent. is cubic, when rolled above 1015 degrees Cent. or when rolled between 450 and 1015 degrees Cent. and heated above 1015 degrees Cent. is hexagonal, and when rolled at room

[10]Howard L. Hopkins is at present a research metallurgist with the U. S. Aluminum Company at Cleveland, Ohio.

temperature is again hexagonal. Cast cobalt, however, is pure hexagonal; on cooling rapidly, therefore, it appears that the high temperature hexagonal phase (gamma) passes into the low temperature hexagonal phase (alpha)—which is identical to it—without passing through the intermediate beta phase. This behavior seems unique.

The reluctance characteristic of the gamma-beta and beta-alpha transformations is not at all surprising. The heat of transformation is apparently quite small (and presumably also the free energy change), the volume change is very small (the space occupied by one atom in the beta phase is 10.83Å^3, and by one atom in the alpha phase is 11.01Å^3.), and the arrangement of the atoms in space is nearly alike. Although the problem has not been completely analyzed it seems quite certain that the transformation proceeds by a Widmanstätten mechanism (Wassermann, above), nuclei of the hexagonal alpha phase forming with the basal (00.1) plane upon and nearly coincident in atom positions with the octahedral plane of the beta phase. Such a transformation mechanism, because of the near identity of the interatomic distances and the near symmetry of the two kinds of lattices, involves but little atom displacement, results in but little distortion, and, accordingly, the velocity of the transition is not catalyzed (or more properly, autocatalyzed) by distortion setting up large numbers of nuclei.

The beta-alpha transformation is thus quite sluggish. It might well be expected, therefore, that Mr. Sykes found no evidence for this transformation in the cobalt-tungsten system,—at least I judge he did not, for I find no mention of such transitions in his paper. Cold working of cobalt-rich alloys, however, might initiate the change and lead to extensive property change. May I ask whether any evidence along this line has been obtained?

Mr. Sykes' excellent photomicrographs offer interesting information concerning the mode of segregation of a phase from a solid solution, a subject so important in the study of precipitation-hardening systems. Figs. 29, 31, 38, 24, 25, 26 all show nicely defined Widmanstätten figures,—Fig. 29 especially. But other structures, not clearly Widmanstätten figures, are no less interesting. The complete study which Mr. Sykes has made on the 30 per cent tungsten alloy affords an opportunity to study the sequence of structural changes with gradually changing heat treatment.

Although these structures may not be wholly comparable (Figs. 31, 32, 38 were taken of samples initially quenched from the beta-field, whereas the remainder were taken of samples presumably furnace-cooled from the beta-field), a gradual structural transition from a well-defined Widmanstätten figure to one in which no Widmanstätten structure (in which indeed the eta-phase cannot be identified with certainty) may be seen. In this latter structure (Fig. 41), however, it seems evident that a deep-seated crystallographic transformation is in process, and since it is with this heat treatment that maximum aging effects are formed, it is a structure well worth crystallographic study. The structures shown in Figs. 39, 40, 41, 42 are distinctly new; the possibility of obtaining such structures in an age-hardening system would appear to make this system—and also the system studied previously by Mr. Sykes, iron-tungsten, iron-molybdenum—particularly suited to a study of the age-hardening mechanism.

It might be noted that the construction of the upper limit of the field (Fig. 1) has through an oversight been incorrectly drawn, for this field must impinge upon the peritectoid horizontal KN in a single point to satisfy conditions of heterogeneous equilibrium.

L. W. KEMPF:[1] Mr. Sykes spoke about the necessity for relapping dies made of about 20-35 per cent tungsten, balance cobalt, after they had been in service for some time. I wonder if this necessity for relapping is not more due to volume changes than to the building up of tungsten oxides as suggested. The hardness of the dies as put into service in quenched and aged condition is given as about C50 to 52 which, according to Mr. Sykes' curves, is about the maximum attainable with this concentration of tungsten. It is quite conceivable that during continuous operation at elevated temperatures, precipitation or agglomeration of the tungsten phase should continue with the possibility of accompanying volume changes.

That the conditions necessary for a decrease in density of these cobalt solid solutions upon aging are present would seem to be indicated by the density measurements of Table VII. It may be noted that the density of the quenched solid solutions is increasingly greater as the tungsten content increases to 35 per cent, than the density computed by the rule of mixtures. This suggests that the density of the quenched alloy might decrease upon continued aging and more nearly approach the density computed from the rule of mixtures as the completely annealed condition is attained.

These phenomena are quite common in age-hardening aluminum alloys. In the process of the aging or operation at elevated temperatures many of the aluminum solid solutions will attain a maximum hardness with little or no change in density but on continued aging will show decreasing hardness and decreasing density.

P. H. BRACE:[2] The author, in his Fig. 1, showed the upper transition point, i.e., allotropic change, in pure cobalt at approximately 1100 degrees Cent. and progressing upward as the tungsten content increases. The magnetic change in pure cobalt occurs in the same temperature region and I am wondering whether or not any investigations have been made to show whether the magnetic change occurs at progressively higher temperatures with increasing tungsten.

Author's Closure

The volume increase suggested by Mr. Kempf is possibly the explanation for the observed changes in the bearing diameter of these dies after prolonged service at elevated temperatures.

I am at present unable to supply any data on the magnetic properties of the cobalt-tungsten alloys since no measurements of this sort were attempted in connection with this investigation, nor, so far as I know, have results of any such measurements been published.

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[1]Aluminum Research Laboratories, Aluminum Co. of America, Cleveland, Ohio.

[2]Manager of metallurgical division of Westinghouse Research laboratories, East Pittsburgh, Pa.

A LOW INTERNAL STRESS HEAT TREATMENT

By Charles W. Briggs

Abstract

The phenomenon of aging is used to increase the strength and hardness of steel. The heat treatment preparatory to aging consists of heating the material just below the critical range and quenching in water. The material is allowed to age either at room temperature or at slightly elevated temperatures for a predetermined time.

The lower the aging temperature the greater the time that is required to reach the maximum hardness, and also the greater the hardness obtained.

Cast steel both in the as-cast and annealed condition shows a large increase in yield point, tensile strength, and hardness without losing much ductility over that as found in the as-cast condition.

Low stress heat treatment can be readily applied to very irregular and intricate castings where the expansion and contraction obtained on heat treatment may result in serious injury to the casting.

THE possibilities of the use of age hardening as a low internal stress heat treatment look exceptionally encouraging when various types of intricate and complex steel castings are considered. The term "low stress heat treatment" is used in referring to heat treatment that takes place below the critical range. The usual type of heat treatment, especially that of hardening, involves the setting up of internal stresses of various magnitudes in steel. These, of course, are due in general to stresses arising from the contraction and expansion of the steel traversing the critical range, because it is often the case that a portion of the object may be contracting while another portion may be expanding. This is especially true in quench hardening. The possibility of the simultaneous existence of contraction and expansion does not exist in the heat treating operation below the critical range, and hence the term low stress heat treatment.

Several noteworthy textbooks, in discussing the hardening of steel, have definitely pointed out that in order to harden steel it is

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, Charles W. Briggs, a member of the society, is associated with the Naval Research Laboratory, Division of Physical Metallurgy, Bellevue, Anacostia, D. C. Manuscript received September 8, 1932.

necessary to heat it above its critical range and then cool quickly, as any attempt at hardening by cooling suddenly from a temperature below its critical range would result in but a very slight, if any, increase of hardness. Just how much latitude is to be placed on the term "very slight" is rather difficult to say. Nevertheless, there is a heat treatment that involves sudden cooling from below the critical range that produces important changes in the physical properties of the steel. This heat treatment takes advantage of those results obtained by the phenomenon of aging. The heat treatment in general is as follows: The specimen is heated to a temperature below the

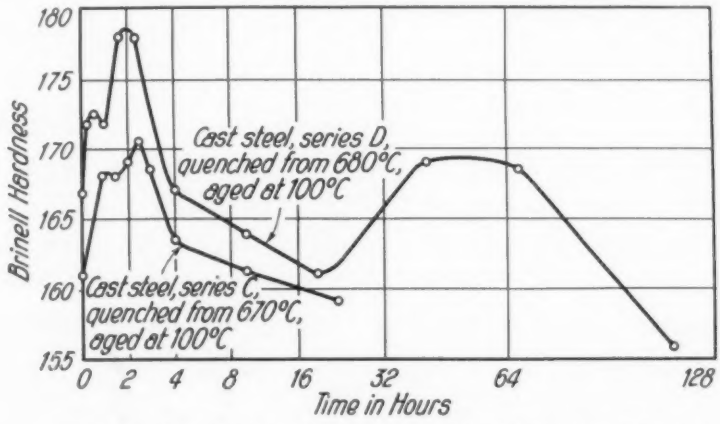


Fig. 1—Cast Steel. Series C, Quenched from 670 Degrees Cent., Aged at 100 Degrees Cent. Series D, Quenched from 680 Degrees Cent. Aged at 100 Degrees Cent.

critical range, preferably between 600 degrees Cent. (1110 degrees Fahr.) and the A_1 point, and quench in water. The specimen is then allowed to age either at room temperature or at slightly elevated temperatures for a predetermined time.

No attempt will be made to go into the mechanism of aging in this article as various investigations have given the subject considerable attention. All that is necessary to point out is that through certain treatments the solid solubility of some of the constituents of steel is increased and upon the duration of time these constituents precipitate out of the solid solubility and in so doing bring about an increase of hardness, tensile strength, yield point; and a decrease of elongation, reduction of area, and impact strength of the steel.

To show these effects a cast steel with the following analysis was used in the experimental work: Carbon 0.25 per cent, manganese 0.70 per cent, silicon 0.34 per cent, phosphorus 0.026 per cent, sulphur 0.028 per cent.

Table I

Series C		Series D		Series E		Series F	
Quenched	670° C.	Quenched	680° C.	Quenched	680° C.	Quenched	680° C.
Aged	100° C.	Aged	100° C.	Aged	50° C.	Aged Room Temp.	
Time	Brinell	Time	Brinell	Time	Brinell	Time	Brinell
As-Annealed	158	As-Annealed	159	As-Annealed	156	As-Annealed	158
As-Quenched	161	As-Quenched	167.2	As-Quenched	164	As-Quenched	166.2
30 minutes	168	15 minutes	171.9	30 minutes	168	1 day	174.3
1 hour	168.8	30 minutes	172.8	1 hour	170.4	3 days	177.2
1½ hours	168	1 hour	170.0	2 hours	170.4	7 days	180.0
2 hours	169	1¾ hours	177	4 hours	171	11 days	181
2½ hours	170.5	2½ hours	177	10 hours	173.4	15 days	183
3 hours	168	4 hours	167	16 hours	175.8	21 days	188
4 hours	163.5	10 hours	163.9	20 hours	176.8	29 days	190
6½ hours	166.0	20 hours	161	28 hours	174.0		
10 hours	161.3	44 hours	169	44 hours	170		
22 hours	159	68 hours	168.5	68 hours	172.6		
		118 hours	155.7	96 hours	174		
				118 hours	172.4		
Hardness		Hardness		Hardness		Hardness	
Increase	12.5	Increase	18.0	Increase	20.8	Increase	32

Brinell hardness test pieces 1 inch by 1½ inches, ¾ inches thick were cut from the cast coupon. Only one Brinell impression was taken on each specimen. The various treatments were given the specimens after which they were rough polished and the Brinell hardness taken. Each reading is the average of 10 measurements. In order to obtain comparable Brinell readings, it was found necessary to anneal the test pieces at 900 degrees Cent. (1650 degrees Fahr.) for 1½ hours before giving the quenching treatment from below the critical range.

The following series of treatments were given:

Series C. Heated for half an hour at 670 degrees Cent. (1240 degrees Fahr.) and quenched in water at room temperature and aged at 100 degrees Cent.

Series D. Heated for half an hour at 680 degrees Cent. (1255 degrees Fahr.) and quenched in water at room temperature and aged at 100 degrees Cent.

Series E. Heated for half an hour at 680 degrees Cent. (1255 degrees Fahr.) and quenched in water at room temperature and aged at 50 degrees Cent.

Series F. Heated for half an hour at 680 degrees Cent. (1255 degrees Fahr.) and quenched in water at room temperature and allowed to age at room temperature.

The Brinell hardnesses as obtained are shown in Table I and are graphically portrayed in Figs. 1, 2 and 3.

In Fig. 1 it will be noticed that the hardness peak comes during

the second to third hour of aging after which there is an over-aging effect followed by a secondary increase in hardness, though of a less magnitude than that obtained within the first 3 hours. A very small hump in the curve during the first hour is recorded. This feature is unexplained as is likewise the secondary hardness fluctuation; however, these features have been prominent in all aging curves recorded by Brinell hardness that have been obtained by the Naval

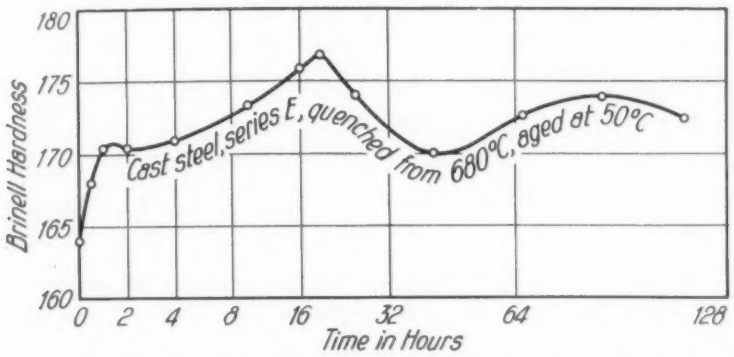


Fig. 2—Cast Steel. Series E, Quenched from 680 Degrees Cent. Aged at 50 Degrees Cent.

Research Laboratory. Herbert in England, using the pendulum hardness tester, has obtained such variations in his aging studies.

Those specimens aged at 50 degrees Cent. show a maximum hardness at about 20 hours, whereas those specimens allowed to age at room temperature show a hardness maximum at about 30 days. This curve continues to rise, but it is so gradual that 30 days can be taken as the proper time to reach the hardness maximum. One of the noticeable features is that the lower the aging temperature, the greater is the time that is required to reach the maximum hardness, and also the greater the hardness obtained.

Table II
Tensile Properties of Aged Steel Castings

Series	Treatment	Tensile Strength Lbs. Per Sq. In.	Yield Point Lbs. Per Sq. In.	Elongation in 2 In. %	Reduction of Area %
A	As cast	77,000	41,500	21.5	32.5
B	Annealed at 900°C	79,000	55,000	25.5	40.2
G	Annealed, quenched from 680°C and aged 20 hr. at 50°C	85,500	63,000	19.7	33.1
	Quenched at 680°C	81,000	50,000	18.0	26.1
H	Quenched at 680°C and aged 2 hr. at 100°C	84,000	51,000	17.5	26.1
	Quenched at 680°C and aged 4 hr. at 100°C	80,750	50,000	19.5	34.7
	Quenched at 680°C	81,500	50,000	17.4	25.8
J	Quenched at 680°C and aged 20 hr. at 50°C	88,400	65,000	15.0	18.1
	Quenched at 680°C and aged 48 hr. at 50°C	85,500	63,000	15.5	24.1
	Quenched at 680° C	81,750	51,000	18.3	28.2
	Quenched at 680°C and aged 21 days at room temp.	87,500	67,000	16.5	20.0
	Quenched at 680°C and aged 30 days at room temp.	90,500	70,500	17.0	21.6

Slight temperature variations just below the critical range produce greater hardness on quenching. This fact is shown well in Series C and D. Thus, in order to duplicate results, the quenching temperature must be accurately observed. Fortunately, however, the duplication of results is not so important as is the increase in hardness, which is comparable for individual aging temperatures.

Figs. 1, 2 and 3 show the correct aging time for maximum hardness. With these points at hand, a minimum number of tensile tests can be made.

In order that the results could refer directly to the as-cast condition, most of the tensile values were taken on the "as-cast" bars, and the low stress heat treatment then performed. Some low stress heat treatments were given cast bars that had been thoroughly annealed. The low stress heat treatment was applied to the 0.505 inch machined specimens. The heating of the specimens at 680 degrees Cent. (1255 degrees Fahr.) was carried on in a nitrogen atmosphere followed by a water quench. The following tests were made:

Series A. As-cast.

Series B. Annealed at 900 degrees Cent. (1650 degrees Fahr.), machined, quenched from 680 degrees Cent. (1255 degrees Fahr.) and aged 20 hours at 50 degrees Cent.

Series G. As-cast, quenched from 680 degrees Cent. (1255 degrees Fahr.) and aged at 100 degrees Cent. for 2 hours and 4 hours.

Series H. As-cast, quenched from 680 degrees Cent. (1255 degrees Fahr.) and aged at 50 degrees Cent. for 20 hours and 48 hours.

Series J. As-cast, quenched from 680 degrees Cent. (1255 degrees Fahr.), aged at room temperature for 21 days and 30 days.

Table II gives the results obtained from tensile testing.

When the low stress heat treatment is applied to the annealed cast steel better ductility properties are obtained. It is likewise again seen that the aging at room temperature produces the greatest tensile strength with an increase of 13,000 pounds per square inch above the "as-cast" value. The yield point increased even more, amounting to 29,000 pounds per square inch. In carrying out heat treating of this type, the aging temperature must be carefully controlled; this can be seen by the fact that by increasing the temperature from 50

to 100 degrees Cent., the aging time drops from 20 to 2 hours, while raising the temperature from 20 to 50 degrees Cent., the aging time is decreased from 30 days to 20 hours. With a temperature of 200 degrees Cent. the age hardening peak is reached in a few minutes.

It was thought that perhaps the physical properties might change after a long period of time even though the aging peak had been reached. For example, after aging at 50 degrees Cent. for 20 hours and then allowing the specimen to stand at room temperature there was a possibility that the hardness might increase after a long

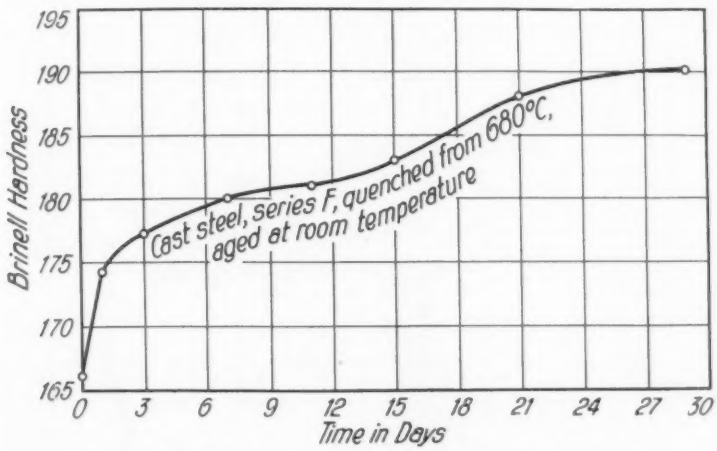


Fig. 3—Cast Steel. Series F, Quenched from 680 Degrees Cent. Aged at Room Temperature.

stand at room temperature so as to approach conditions as obtained by simply aging at room temperature. Or again, having reached the maximum hardness at 20 hours at 50 degrees Cent., there was the possibility that the specimen might soften if it were allowed to stand at room temperature. To answer these questions, specimens after aging were allowed to stand six months. Hardness readings were again taken, with the result that there were no changes in Brinell hardness. In other words, the physical properties obtained from the aging treatment are permanent.

Low stress heat treatment can be readily applied to very irregular and intricate castings where the expansion and contraction obtained on heat treatment may result in serious injury to the casting.

Fig. 4 shows a typical dilation curve of a low carbon steel as recorded by Publow, Heath and Batchelor's Bulletin 41, "Observations on the Dilation of Several Common Steels," Michigan State College, Michigan Engineering Experiment Station. In a normal

hardening operation, the cast steel implement expands uniformly until it reaches the critical temperature at which point contraction takes place followed by a period of arrested contraction and then by more contraction at the A_3 point with subsequent expansion to the temperature of 900 degrees Cent. (1650 degrees Fahr.). Upon quenching from this temperature, the implement must contract to the Ac_3 point, expand to the Ac_1 point and then contract to room temperature. With the nonuniform temperature condition existing in rapidly cooled castings, one portion of the casting may be contracting, and possibly contracting with different rates, while another portion is expanding. Under such circumstances, stresses are set up

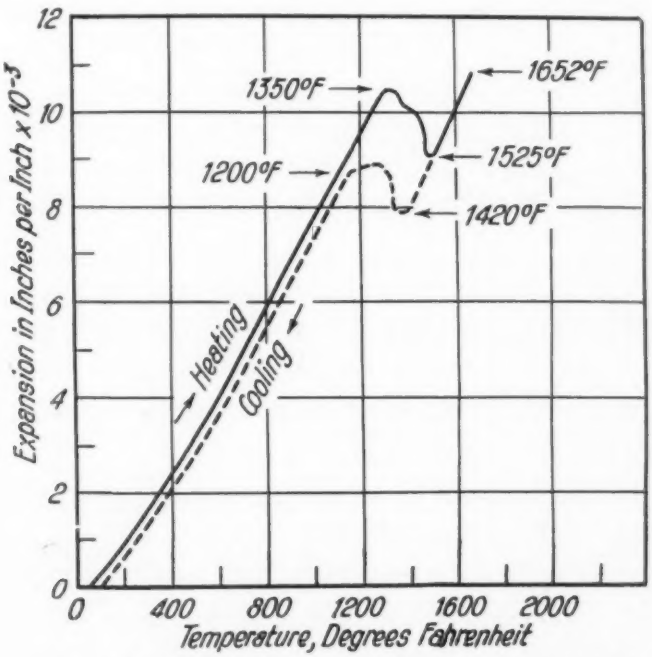


Fig. 4—Dilatation Curve of Unannealed Low Carbon Steel.

within the casting of such magnitudes that cracking takes place. If, however, we quench from below the critical temperature, the contraction rate is practically uniform and stresses resulting from contraction are of minor importance and will not produce cracks.

In cases where more ductility is required in an intricate casting than will be found in it as it leaves the mold, an annealing treatment preceding the low stress treatment should first be given. The heating and likewise the cooling temperature of the casting should be varied slowly in order that there may be no temperature gradient throughout the casting while in the neighborhood of the critical

range. Thus we eliminate possible stresses arising from nonuniform contraction and expansion. Castings so treated will not have as high a tensile strength as the casting that received only the low stress treatment, but the ductility will be more improved. These facts were pointed out in the experimental data. An annealed specimen which was given the low stress heat treatment with an aging time of 20 hours at 50 degrees Cent. had a tensile strength of 85,500 pounds per square inch and a reduction of area of 33.1 per cent while the "as-cast" specimen with the identical low stress heat treatment gave 88,400 pounds per square inch tensile strength and 18.1 per cent reduction in area. From this it is seen that it would be definitely better to use an annealing treatment previous to the low stress heat treatment, as in this manner the dendritic structure is broken up by recrystallization. However, in some cases this cannot be done due to casting warpage and uneven heating that may possibly exist on annealing which might be detrimental to an intricate casting.

Summary

1. Important changes in the physical properties of steel can be obtained by a low internal stress heat treatment, which involves quenching from below the critical range followed by aging.

2. Low stress heat treatment allows for the heat treating of intricate castings which would otherwise fail by normal quenching and possibly normalizing treatment because of the formation of contraction and expansion stresses.

DISCUSSION

Written Discussion: By Horace C. Knerr, consulting metallurgical engineer, Philadelphia.

Mr. Briggs' paper is of great technical interest in illustrating a characteristic of steel heretofore generally overlooked. The hardening phenomenon demonstrated by his tests is due presumably to a solution and precipitation action resulting from a small solubility of carbon and other elements or compounds thereof below the critical A_1.

It has, of course, been well known that carbon or carbide is slightly soluble below the critical range and that this solubility increases with temperature. This accounts for the growth of carbide particles in quenched steel when tempered and which is accompanied by decreased hardness resulting from the decreased keying effect of the larger particles.

The hardening shown in Briggs' experiment is very much less than the hardening producible in alloys such as duralumin whose hardening is entirely due to solution and precipitation effects. It seems reasonable to expect that considerably greater sub-critical hardening might be obtained in iron alloys by

the introduction of hard compound-forming elements whose solubility below the critical temperature was greater than that of the elements ordinarily found in steel, but which were comparatively insoluble at ordinary temperatures.

The question arises, however, whether any sub-critical hardening effect producible in steel would be of much importance as compared with the very great hardening obtainable by oil quenching from above the critical range. The advantages which may accrue from sub-critical quenching are open to question. Mr. Briggs implies that water quenching of a casting from below the critical range is less apt to produce strains or cracking even than normalizing from above the critical range. One wonders whether this is actually the case. The mild air cooling or normalizing from above the critical range is well known to have very substantial hardening and strengthening effects upon castings of the composition range referred to. Such normalizing has the advantage of removing internal strains which may have been present and if properly done is likely to produce no serious strains as a result of the treatment. On the other hand, to quench a bulky casting from approximately 1250 degrees Fahr. or a dull red heat, into water, would presumably set up some very severe contraction stresses and as the metal itself has a very much reduced strength at that temperature, might readily cause serious deformation or even rupture. It is well known to those accustomed to the heat treatment of duralumin and similar alloys that very serious distortion often occurs in them due to such quenching.

Written Discussion: By C. R. Austin, section engineer, alloys and process section, research laboratories, Westinghouse Electric and Mfg. Co., East Pittsburgh.

The paper by Mr. Briggs on the sub-critical hardening of low carbon steels is of considerable interest and possible practical importance, and the data which he presents show a very marked increase in the yield point and tensile strength with very little corresponding loss of ductility as revealed by the tensile test. I believe that in steels showing a relatively low elongation in the unaged state, the impact test reveals more clearly any marked loss in "service ductility" of the metal. No other test appears to furnish so good a criterion on changes in this property.

This is well illustrated in the paper presented by the speaker earlier this morning. Thus by normalizing a fabricated steel the yield point was raised from 67,000 to 75,000 pounds per square inch, with little or no change in the elongation (about 26%). The Izod impact was profoundly affected because this increase in yield was accompanied by an increase in Izod value of about 13 foot-pounds (4½ to 17½ foot-pounds). It would be of considerable interest to have impact data furnished by the author of the paper on these steels.

Mr. Briggs very properly emphasizes the importance of the production of internal stresses of various magnitudes by the usual type of heat treatment, particularly those stresses induced by volume changes during rapid cooling through the critical ranges. Where localization of stress is possible there is a marked tendency to incipient cracking. This dilatation of steel is the bane of the designer of intricate shapes or of large castings.

The age hardening of alloys is also associated with volume changes, and although the aging discussed in the present paper is probably accompanied by

only slight dilatation, the importance of the work would be enhanced if the author could supplement his data with information on the relative dilatation due to transformations and to age hardening.

As the effect of aging on the physical properties was obtained on small samples it is of importance to check the effect of quenching rates on subsequent aging. Possibly Mr. Briggs can give us some information on this point. The property of aging, of course, depends on a decrease in solid solubility with falling temperature. It is necessary to cool sufficiently quickly after annealing just below the lowest critical temperature to retain certain constituents in solid solution. It would appear at first sight that at the relatively low temperature of pre-anneal the rate of cooling was not critical. However, the data included in the paper indicate that the effects of age hardening are evident after only a few minutes at 100 degrees Cent. This would suggest that rapid cooling at 600 degrees Cent. was necessary to effectively retain solution of the aging constituents.

In general, the findings of Mr. Briggs agree with those published by E. W. Ehn where the hardening is considered to be due to carbon. However, Ehn gives data to show that with three carbon steels containing 0.044, 0.028, and 0.12 per cent of that element, the higher the carbon content the lower the hardening effect on aging at room temperature. He does not attempt to explain these facts but he does state that quenching must be rapid in order to obtain the maximum amount of the unstable phase in solid solution. It would naturally be presumed, therefore, that in order to bring out the important increases in tensile properties noted in the paper, a rapid rate of cooling throughout the steel casting might be necessary.

The author is to be congratulated on bringing what is practically a new phase of an old subject before this society.

C. H. HERTY, JR.:[1] I would like to say a few words about Mr. Briggs' paper.

We have been doing a good deal of work on quench aging of low and medium carbon steels in the rolled state. We find, for example, that as the carbon increases in the forged steel or rolled steel the aging effect decreases very rapidly so that when you get up to 0.30 or 0.40 per cent carbon there is practically no aging from the 700 degrees Cent. quench.

However, in Mr. Briggs' cast steel you do get it. As soon as I received the paper I took a piece of rolled steel of approximately the same analysis as that reported in the paper and gave it the treatment that Mr. Briggs gave and got no aging effect over a period of 10 days at 30 degrees Cent.

It seems to me that those two things are very important if you would look for the cause of aging.

In cast steel the structure is larger than in a rolled steel, and it does have an opportunity for precipitation of carbon. On account of the small crystal size, such an opportunity does not exist in the rolled steel. In other words, when a quantity of steel is solidified terrific micro segregation of carbon exists, and the analysis of the edge of a grain must be greatly different from the

[1]Director of research, mining and metallurgical advisory boards, Carnegie Institute of Technology, Pittsburgh.

analysis of the center of the grain. I believe it is on this point that the aging of cast steel depends. I think if you look at Mr. Briggs' paper not only from the standpoint of the ability to increase the tensile strength of the castings but also from the standpoint of the mechanism of aging, you will see that he has presented some very valuable information.

I hope in Mr. Briggs' closing remarks he will make some reference to his own views on the nature of the elements or compounds which are being taken into solution by the quench and precipitated in a critical dispersion by the subsequent aging treatment, and also what relation these materials might have to the aging initiated by cold work of medium carbon steels.

Author's Closure

In regard to quenching rapidly, it is quite true that the faster the quench the greater the age hardening. However, in this paper we were discussing more or less intricate castings with thin-walled sections, and in that case the quench will be rather rapid.

I do not think it would be worth while to attempt to use any such heat treatment on a large casting of rather thick cross section.

Of course, it must be remembered, too, that several foundrymen use high carbon steel as they claim that they are able to pour thinner sections. This, of course, would limit the aging effect and the aging treatment would not be necessary because a high tensile strength is already present. There are also other foundrymen who claim that by superheating a very low carbon steel and pouring it, there are less tendencies for internal hot tears forming. In this case the aging treatment would come in handy.

I should very much like to answer Dr. Herty's question as to the underlying theory of aging and the elements that are influential in bringing about the phenomenon of age hardening in steel, but I am very certain it is not at all as simple as Mr. Knerr attempted to portray. Experiments at the Naval Research Laboratory and the published works of Sacks, Koster, and others have definitely shown that the problem is a most complicated one. I think that the best summary on the subject has been prepared by Dr. R. F. Mehl.

He shows that in general the aging effect may be due to carbon, oxygen, nitrogen, sulphur, or perhaps a combination of these elements.

In reply to Mr. Knerr's comparison of sub-critical hardening effect to that of oil quenching, I merely point out that it is comparable and that there is a lower internal stress involved, and that intricate pieces stand up better under such a treatment than they do under a normalizing treatment. It is admitted that the process has its applications and it is rather difficult to see how it would sufficiently improve a bulky casting.

Dr. Austin's suggestion that impact values be studied is a very good one. A dilatation study would likewise prove interesting. In answer to Dr. Austin's question on cooling rates it may be said that an ordinary water quench produces practically maximum results. A brine quench produces only a slight additive age hardening effect. Slower cooling than that produced by a water quench tends for reduced age hardening effects and thus thin sections are ideal for this type of processing.

OBSERVATIONS ON THE EFFECT OF NORMALIZING MEDIUM MANGANESE STEELS ON THE MICRO-STRUCTURE AND PHYSICAL PROPERTIES

By C. R. Austin

Abstract

The paper presents data obtained from a study of the effects of various normalizing treatments on the microstructure and mechanical properties of a steel containing 1.5 per cent manganese and about 0.4 per cent carbon. Comparisons are drawn between values obtained for the yield point, the endurance limit, and the Izod impact strength, from samples as hot-rolled, ordinary normalized and double normalized. The importance of the normalizing treatment is demonstrated by the increase in the endurance limit and in the Izod impact strength.

In an appendix to the paper data are presented to illustrate the profound effect of slight increases in the manganese and carbon content of these "pearlitic manganese steels." The metallography and effects of heat treatment on the resistance to impact of a steel containing 0.63 per cent carbon and 1.8 per cent manganese are given.

The observations indicate the need for carefully studying the chemical analysis of medium manganese steels before adopting for some specific service.

EARLY researches on medium manganese steels lead to the generally accepted idea that such steels were brittle to work and that they had not sufficient toughness for commercial application. An interesting account of the developments, properties and applications was recently given by E. E. Thum.[1] Probably by far the greatest tonnage of the steel finds its application in the fabrication of rails and of high strength seamless tubing, and to high strength castings.

The present paper deals with steels containing about 0.4 per cent carbon and up to about 1.6 per cent manganese, and considers the properties and metallography of commercial steels which have found

[1] E. E. Thum: "The New Manganese Steel Alloys," *Proceedings*, American Society for Testing Materials, Vol. 30, 1930, Part II, p. 215.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, a member of the society, is section engineer, alloys and process section, metallurgical division, Westinghouse Electric and Manufacturing Company, East Pittsburgh. Manuscript received April 22, 1932.

their way into industry for certain applications where high strength and moderate toughness were essential.

By increasing the manganese content to about 1.5 per cent it is considered that this brings the steel into the range of true alloy steels, and it is generally recognized that in order to benefit materially by the introduction of special alloying elements, the steel should be subjected to some form of heat treatment.

Undoubtedly the optimum in physical properties can be obtained by a quenching and tempering treatment, but there are always practical difficulties and economic reasons tending to deter the handling of large masses of steel in this manner. It was considered of interest to conduct some experiments to ascertain what properties these medium manganese steels were capable of yielding from some form of normalizing treatment.

The metallographic structure of these steels "as-rolled" is rather coarse and the low single blow impact values obtained are to be anticipated. Although it is true that the exact significance of the various failure tests is not well understood, there seems little doubt that an increase in the Izod impact values accompanied by no loss of strength of the steel would be very desirable.

It was from such considerations that the writer was led to initiate a brief research on medium manganese steel directed to the following objectives:

1. To determine the best combination of mechanical properties of medium manganese steels, having the composition cited, which can be obtained by some simple normalizing treatment.

2. To demonstrate the superiority in such properties of a properly normalized steel over the same material put into service in the "as-rolled" condition.

Material Tested

Preliminary experiments were conducted on a steel containing 1.57 per cent manganese and 0.42 per cent carbon. Lack of material, however, demanded that all the physical tests be made on a steel having the following composition:

	Per Cent
Carbon	0.40
Manganese	1.40
Phosphorus	0.012
Sulphur	0.036
Silicon	0.28

The material was in the form of 6⅝ inch diameter pipe with 0.33 inch wall, in the hot-rolled state.

Preliminary Investigation

Among the physical data collected on this type of manganese steel in the hot-rolled state, it appears that the Izod impact values permit the greatest improvement. It has been indicated that the metallographic structure of these steels tends to be coarse and it was considered that an analysis of the effect of various simple heat treatments on the microstructure would most rapidly suggest the optimum conditions of treatment to yield a fine grain, improved Izod values and generally satisfactory physical properties. The investigation therefore naturally consists of two sections:

1. A metallographic study on the effect of heat treatment on the structure of the steel.
2. Physical test data on the steel, heat treated in the manner indicated as most satisfactory from the metallographic study.

Metallographic Study

This phase of the work consisted of a correlation of the effect of normalizing at different temperatures with the metallographic features observed. The experiments were conducted on the 1.57 per cent manganese and 0.42 per cent carbon steel.

In order to determine the lower limiting temperature for normalizing, small specimens were cut for thermal analysis. The maximum temperature to which the samples were heated did not appear to have any marked effect on the location of the critical points. On heating, the heat absorption occurred at 734 degrees Cent. (1355 degrees Fahr.). The results from cooling showed a small point above the main heat evolution. The results are given in Table I.

Table I

Specimen	Heating		Cooling	
	Small Point Degrees Cent.	Main Point Degrees Cent.	Small Point Degrees Cent.	Main Point Degrees Cent.
1	725	734	650	632
2	...	...	664	635
3	...	734	654	*645

*Recalesced from about 630 degrees Cent.

Thus the carbide transformation on heating occurred at about 735 degrees Cent. and on cooling at about 650 degrees Cent. (1200 degrees Fahr.). We are concerned only with the former. Varying the rate of heating appeared to have little effect on the location of the Ac point (735 degrees Cent.). This is important and indicates that, say, 740 degrees Cent. (1365 degrees Fahr.) is the minimum temperature of true normalizing, and that this temperature is independent of the rate of heating. The 1.40 per cent manganese, 0.40 per cent carbon steel did not reveal any marked difference in thermal characteristics.

Small samples were cut from the 1.57 per cent manganese steel and normalized at different temperatures and for varying periods of time, and then prepared for hardness determinations. The temperatures ranged from 750 to 950 degrees Cent. (1380 to 1740 degrees Fahr.) and the periods of anneal from 15 to 60 minutes and in one case up to 5.5 hours. Twenty-five tests were made in this manner, but the data is not included as the hardness figures were not sufficiently regular to attempt to deduce much useful information from them.

These same samples were therefore polished and prepared for metallographic examination in order to determine what heat treatment might be expected to yield the best mechanical properties. Details of these experimental observations will not be recorded but a resumé of the general observations is given.

1. In the hot-rolled state the material has a fairly uniform large grain.
2. In the normalized condition, as the temperature of normalizing is raised, the general grain size is increased and the banded structure effect is decreased.
3. As the time of normalizing at any given temperature is increased, the general grain size is increased to only a small degree.
4. The higher the temperature of normalizing the greater the apparent amount of free ferrite separating.
5. The general microstructure of all samples is sorbito-pearlite.
6. With any ordinary normalizing treatment, it is difficult to avoid a considerable variation in grain size even over small sectional areas.

7. The samples were most suitably etched by using a mixture of 5 per cent picric acid and 2 per cent nitric acid in alcohol.

Double Normalizing

A careful consideration of the metallography of these tests led to the idea of "double normalizing" the steel. By this term is meant an ordinary normalizing treatment at some given temperature followed by the usual air cooling, with a subsequent normalizing at the same or some other temperature, again followed by air cooling.

This idea was considered and experimented upon because these medium manganese steels were found to be not readily susceptible to ordinary normalizing in the manner noted in plain carbon steels.

The metallographic structure desired was one showing an elimination of the banded structure, the presence of little free ferrite and a uniform but fine grain. The temperatures of primary normalizing investigated ranged from 775 to 900 degrees Cent. (1425 to 1650 degrees Fahr.), and those of secondary normalizing 735 and 750 degrees Cent. (1355 and 1380 degrees Fahr.).

The correct annealing temperature to provide the above mentioned structure was found to consist of heating periods of about 30 minutes at 775 degrees Cent., or possibly 800 degrees Cent. (1470 degrees Fahr.), followed by a second anneal at 750 degrees Cent. Both treatments were followed by air cooling.

Examples of the effects of various heat treatments on the metallographic structure are given in Figs. 1 to 7 inclusive. These provide a general picture of the types of structure encountered during the investigation.

Fig. 1 is representative of the hot-rolled material. Fig. 2 illustrates the results of normalizing at too high a temperature, 950 degrees Cent., whereby a coarse and irregular grain is formed accompanied by considerable ferrite separation. Fig. 3 shows the persistence of the banded structure in parts of the sample after normalizing at 750 degrees Cent. (1380 degrees Fahr.).

Figs. 5 and 6 present the optimum conditions obtained by "double normalizing." The elimination of the banded structure and the presence of a fine uniform grain is evident. Fig. 7, showing the metallographic features of a specimen normalized in the usual manner at 800 degrees Cent. (1470 degrees Fahr.), is included for purposes of comparison. It is of interest to point out that the structure shown

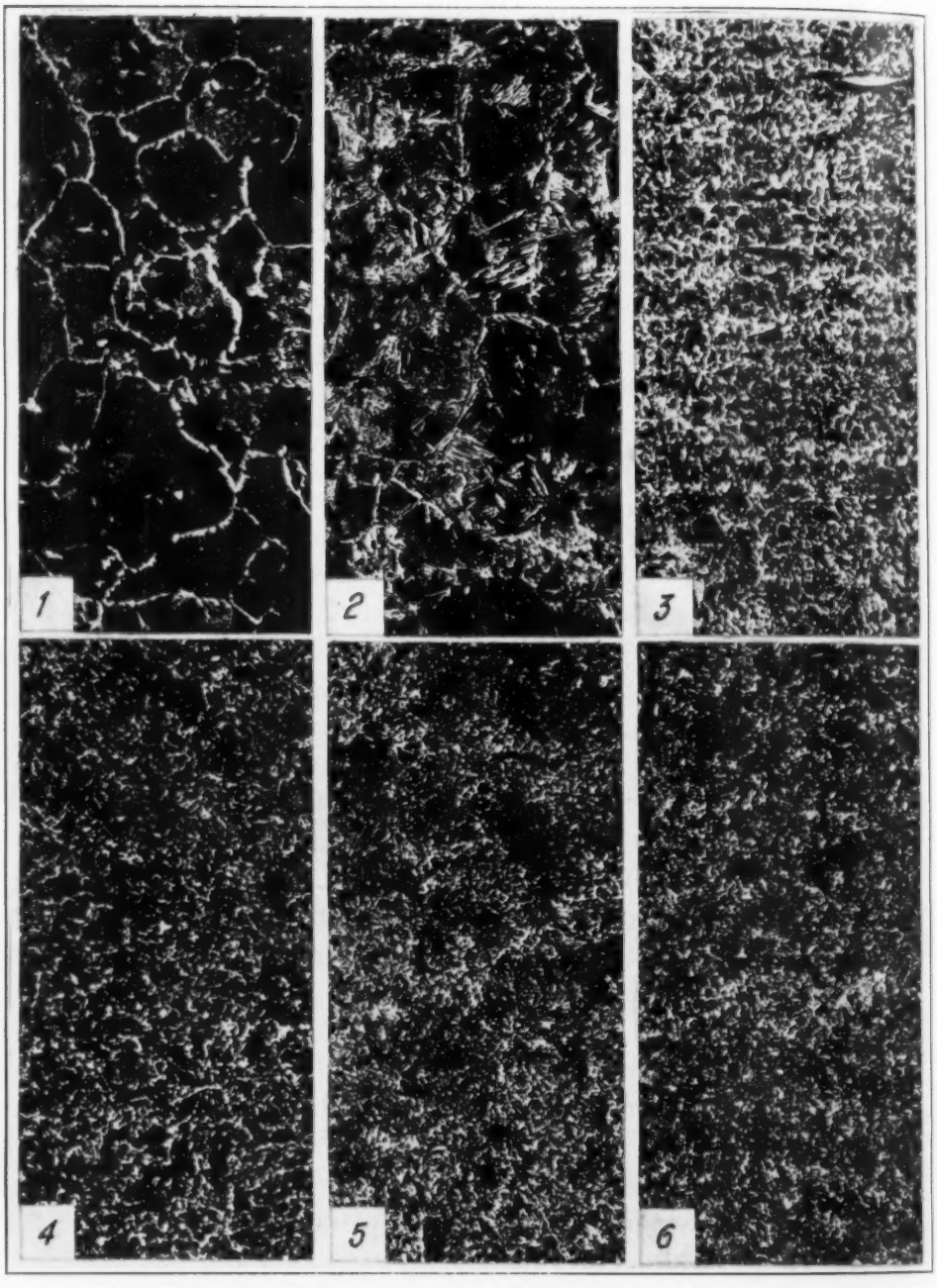


Fig. 1—Steel in the Hot-Rolled Condition. Etchant—5 Per Cent Nitric, 2 Per Cent Picric Acid in Alcohol. × 100.

Fig. 2—Annealed 30 Minutes at 950 Degrees Cent., Air-Cooled. Large Grain and Ferrite Separation Caused by too High a Normalizing Temperature. × 100.

Fig. 3—Annealed 30 Minutes at 750 Degrees Cent., Air-Cooled. Illustrates the Banded Structure Found in Certain Sections of the Samples. Picric-Nitric Acid Etchant. × 100.

Fig. 4—Same Specimen as in Fig. 3, Showing Absence of Banded Structure. × 100.

Fig. 5—Double Normalized at 775-750 Degrees Cent. This Steel is Very Fine-Grained. The Dark Patches are Due to an Etching Effect. Etchant Same as Fig. 3. × 100.

Fig. 6—Double Normalizing at 800-750 Degrees Cent. Fine-Grained Structure Free from Banding. Etchant Same as Fig. 3. × 100.

in Fig. 6 was identical to that shown in Fig. 7, before the second normalizing treatment.

Mechanical Tests

In order to determine if the aforementioned metallographic observations had any real significance so far as physical properties were concerned it was decided to duplicate some of the experimental anneals on Izod impact specimens. It will be recalled that it was considered that an impact test would most readily reveal any change in physical characteristics of the steel.

Oversize Izod test pieces were machined from the 1.57 per cent manganese steel and given a single or double normalizing treatment to obtain comparison data. The samples were machined to size, notched and tested. The complete data is presented in Table II.

Table II
Izod Impact Values

Sample No.	Heat Treatment	Izod Impact Foot-pounds to Fracture	Brinell Hardness No.
1 and 3	30 mins. at 750° C.	6.8 and 6.6	220 and 208
2 and 4	30 mins. at 800° C., then 30 mins. at 750° C.	24.4 and 25.8	223 and 218
5 and 7	30 mins. at 800° C.	18.8 and 18.5	223 and 217
6 and 8	30 mins. at 775° C., then 30 mins. at 750° C.	26.0 and 25.0	217 and 207
9 and 11	30 mins. at 850° C.	7.2 and 8.7	229 and 226
10 and 12	30 mins. at 850° C., then 30 mins. at 750° C.	17.0 and 19.5	204 and 207

The results indicate the marked advantage of the double normalizing treatment in effect on impact resistance.

In order to determine whether the high Izod impact values obtained by the double treatment were accompanied by satisfactory tensile and yield point properties, and that such Izod values could be obtained on normalizing larger sections of the material, suitable sections were prepared and heat treated as previously described.

All material subsequently described under the present heading contained 1.4 per cent manganese and 0.40 per cent carbon. The test pieces were cut about 18 inches long and 3 inches wide from ⅓ inch thick steel, and heat treated in that form. Microsections were cut from tests representing each normalizing treatment to serve as a check on the structure, and after the second normalizing treatment a strip was cut to provide two impact test pieces. The remainder of the 18-inch strip was machined for tensile test. The heat treatment was given to six samples in the following manner:

Table III
Tensile Properties with Double Normalizing

Specimen No.	Yield Point Pounds per Square Inch	Ultimate Pounds per Square Inch	Per Cent Elongation 2"	Per Cent Elongation 8"	Per Cent Reduction of Area
1	78,510	113,520	33.5	15.6	49.5
2	76,300	111,600	35.0	16.5	48.9
3	70,180	109,010	30.0	13.8	50.6
4	70,900	110,630	33.0	14.8	49.2
5	71,680	109,600	....*	9.3*	39.3
6	70,170	109,320	34.5	15.5	50.2

*These figures are unreliable as the specimen broke in the gage mark.

Specimens 1 and 2—anneal 30 minutes at 800 degrees Cent., air cool; anneal 30 minutes at 750 degrees Cent. and air cool.

Specimens 3 and 4—anneal 30 minutes at 775 degrees Cent., air cool; anneal 30 minutes at 750 degrees Cent. and air cool.

Specimens 5 and 6—anneal 30 minutes at 850 degrees Cent., air cool; anneal 30 minutes at 750 degrees Cent. and air cool.

The results of tensile tests are recorded in Table III.

The 800-750 degrees Cent. double normalizing appears to result in a marked improvement in yield point values. The tensile strength and ductility is satisfactory in all tests. The results of the impact tests are given in Table IV.

Table IV
Izod Impact Values with Double Normalizing

Specimen No.	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	6A	6B
Foot-pounds to Fracture	28.4	35.1	25.4	29.2	31.5	23.5	26.8	26.9	23.7	25.2	22.5	24.9
Average Izod Value	31.7		27.3		27.5		26.8		24.5		24.9	

It is noted that all these tests proved very satisfactory, and that a good impact strength was obtained with any of the above double heat treatments. For purposes of comparison, it was desired to have similar data on specimens single normalized under the same conditions as for double normalizing, and also to have data from the "as-rolled" steel. The data obtained from a single normalizing treatment again referred to the 18-inch strip, and heat treatment was given six samples in the following manner:

Specimens 7 and 8—anneal at 750 degrees Cent. for 30 and 60 minutes respectively.

Specimens 9 and 10—anneal at 800 degrees Cent. for 30 and 60 minutes respectively.

Specimens 11 and 12—anneal at 850 degrees Cent. for 30 and 60 minutes respectively.

Each specimen gave 2 Izod tests and one tensile test.

The data are tabulated in Tables V and VI.

Table V
Tensile Properties with Single Normalizing

Specimen No.	Yield Point Pounds Per Square Inch	Ultimate Pounds Per Square Inch	Per Cent Elongation 2 Inches	Per Cent Elongation 8 Inches	Per Cent Reduction Area
7	69,230	111,530	32.5	15.3	48.0
8	67,910	111,990	33.0	15.4	47.0
9	75,040	116,020	29.5	12.6	42.1
10	74,450	115,840	27.0	11.3	35.4
11	71,480	114,150	28.5	12.3	44.7
12	74,090	116,830	28.0	12.4	35.7

Table VI
Izod Impact Values with Single Normalizing

Specimen No.	7A	7B	8A	8B	9A	9B	10A	10B	11A	11B	12A	12B
Foot-pounds to Fracture	14.0	8.0	12.5	18.7	20.3	16.1	15.2	15.9	15.2	12.2	10.0	14.5
Average Izod Value	11.0		15.6		18.2		15.6		13.6		12.3	

It will be noted that the impact values are rather irregular. A comparison between tensile and impact values for the "as-rolled," single and double normalized steel is readily obtained by reference to Table VII.

Table VII
Illustrating Effects of Different Heat Treatments on Properties

Heat Treatment	Yield Point Pounds Per Square Inch	Ultimate Strength Pounds Per Square Inch	Per Cent Elongation 2"	Per Cent Elongation 8"	Per Cent Reduction in Area	Izod Impact Values Foot-pounds to Fracture	Average	
As-rolled	67,070	116,180	27.5	12.8	41.8	4.3	4.3	...
	68,560	117,420	24.0	11.5	33.3	4.5	5.0	4.5
Single normalized	75,040	116,020	29.5	12.6	42.1	20.3	16.1	...
	74,400	115,840	27.0	11.3	35.4	15.2	15.9	16.9
Double normalized	78,510	113,520	33.5	15.6	50.6	28.4	35.4	...
	76,300	111,600	35.0	16.5	49.2	25.4	29.2	29.6

In Table VII the optimum values for yield point in the different heat treatments have been recorded with the corresponding values for

impact. The marked increase due to double normalizing in the resistance to failure by impact shock is evident.

Fatigue test data were also collected on the double normalized steel. Results obtained by use of the R. R. Moore type of machine are given in Table VIII. Comparison may be made with previous data available on rolled material.

Table VIII

Fatigue Data on Double Normalized and Hot-Rolled Steel

Pounds Per Square Inch Stress	As-Rolled
67,000	Failed at 73,800 reversals
64,000	Failed at 137,900 reversals
61,000	Failed at 290,200 reversals
58,000	Failed at 374,300 reversals
55,000	Failed at 879,500 reversals
52,000	Did not fail at 25,679,500 reversals
52,000	Failed at 3,954,400 reversals
52,000	Failed at 1,688,000 reversals
51,000	Did not fail at 36,630,000 reversals
51,000	Failed at 13,914,900 reversals
Pounds Per Square Inch	**Double Normalized**
70,000	Failed at 32,800 reversals
69,000	Failed at 102,400 reversals
64,000	Failed at 183,100 reversals
63,000	Failed at 308,100 reversals
62,000	Failed at 314,000 reversals
61,000	Failed at 410,000 reversals
61,000	Did not fail at 10,170,000 reversals
61,000	Did not fail at 10,480,000 reversals
60,000	Did not fail at 10,079,000 reversals
58,000	Did not fail at 12,084,000 reversals

There is much more scattering in the values from the "as-rolled" steel. The endurance limit was taken as 51,000 pounds per square inch for the as-rolled steel and 61,000 pounds per square inch for the double normalized samples. No data were specifically prepared for single normalizing on this test, but some data which were available on a similar steel have been included in the comparison tabulation below.

Table IX

Comparison of Fatigue Data and Endurance Ratio

Heat Treatment	Ultimate Strength Pounds Per Square Inch	Yield Point Pounds Per Square Inch	Per Cent Elongation in 2 Inches	Endurance Limit	Ratio
As-rolled	116,680	67,240	18.5	51,000	0.440
Double Normalized	112,600	77,400	32.2	61,000	0.543
0.44C 1.44 Mn As-rolled	113,230	64,180	17.8	49,000	0.424
Single Normalized	109,840	67,800	21.2	52,000	0.473

Conclusions

The so-called medium manganese steels are frequently referred to as "pearlitic manganese steels." Consideration of the microstructure in the "as-rolled" or normalized condition suggests that the structure is sorbitic rather than pearlitic, and that it is this fine sorbitic structure to which the steels owe their high strength. The profound effect of only small further additions of carbon and manganese to the steels discussed in this paper will be illustrated in the appendix.

The amenability of these steels to important structural changes by simple heat treatments has been illustrated in the photomicrographs. The double normalizing treatment results in the formation of a very fine grain, an elimination of the banding structure, and in the rejection of free ferrite from the solid solution in small and well distributed particles.

The effect of this type of treatment on the tensile properties, on the Izod impact resistance values, and on the endurance limit of the steel has been demonstrated. Comparing only the double normalizing values with the "as-rolled" properties (and the "as-rolled" condition is commercially regulated to provide as close an approximation to regular normalizing as practicable), the tensile yield is raised from 68,000 to 78,000 pounds per square inch by heat treating. Similarly the Izod values are raised from 4.5 to nearly 30 foot-pounds and the fatigue values from 51,000 to 61,000 pounds per square inch.

A marked improvement over single normalizing is also noticed in the data for the double normalized tests in both impact and resistance to fatigue. Further, the double treatment is not so critical as regards temperature and a definitely more uniform product appears to accrue.

Appendix

This appendix provides data illustrating the profound effect of slight increases in the manganese and carbon content of these "pearlitic manganese steels" and presents data on the metallography and resistance to impact of a heat treated steel containing 1.8 per cent manganese and 0.63 per cent carbon. In order to determine the optimum conditions for a normalizing treatment, a thermal analysis of this steel was made. The heating curve showed a good thermal arrest at 725 degrees Cent. (1340 degrees Fahr.).

Effect of Annealing Above the Critical Point of the Steel

Several small samples of the steel were cut for observation of the effect of heating on the microstructure. The heat treatment consisted of heating a sample in vacuo to the desired temperature, maintaining for 30 minutes or two hours, and cooling in still air. Vacuum annealing was used to ensure eliminating decarburization effects.

Fig. 8 illustrates the microstructure of the steel in the hot-rolled condition, and Figs. 9 to 14 illustrate some of the microstructures observed after the heat treatment indicated under each photomicrograph.

A thirty minute anneal at 750 degrees Cent. (1380 degrees Fahr.) leads to a pronounced banding in the structure (Fig. 9). At 800 degrees Cent. (1470 degrees Fahr.) this is more marked (Figs. 10 and 11), and at 850 degrees Cent. (1560 degrees Fahr.) shown in Fig. 12 the appearance of the light areas is so much developed as to lead to an apparent disappearance of the banding effect.

In plain carbon steels this banding or striation of the structure is usually ascribed as due to the presence of bands of free ferrite in the steel, which have rejected most of the carbon. This phenomenon is variously explained as due to sulphur, phosphorus, manganese or oxygen concentration. In this medium manganese steel it is noted that those bands are not ferrite, but that they present an acicular or pseudo-martensitic structure. After annealing at 1000 degrees Cent. (1830 degrees Fahr.) and air cooling, ninety per cent or more of the steel has this acicular structure (see Fig. 14). All these photomicrographs were taken from the center of the heat treated specimens. Reference must also be made to the cracks found in two of the specimens. In the upper part of Fig. 10 minute cracks can be observed in the pseudo-martensitic material. More pronounced cracking can also be seen in Fig. 11. These cracks were not detected in the unetched specimens.

The Rockwell hardness of some of these specimens was measured and conversion figures obtained for the Brinell hardness and tensile strength of the steel, deduced from the information given in the Bureau of Standards Bulletin Paper No. 334.

From a consideration of the microstructure and the tensile strength of the steel after heating to various temperatures above the highest critical point and air cooling, it is clear that this material is not amenable to normalizing in the generally accepted sense of heat

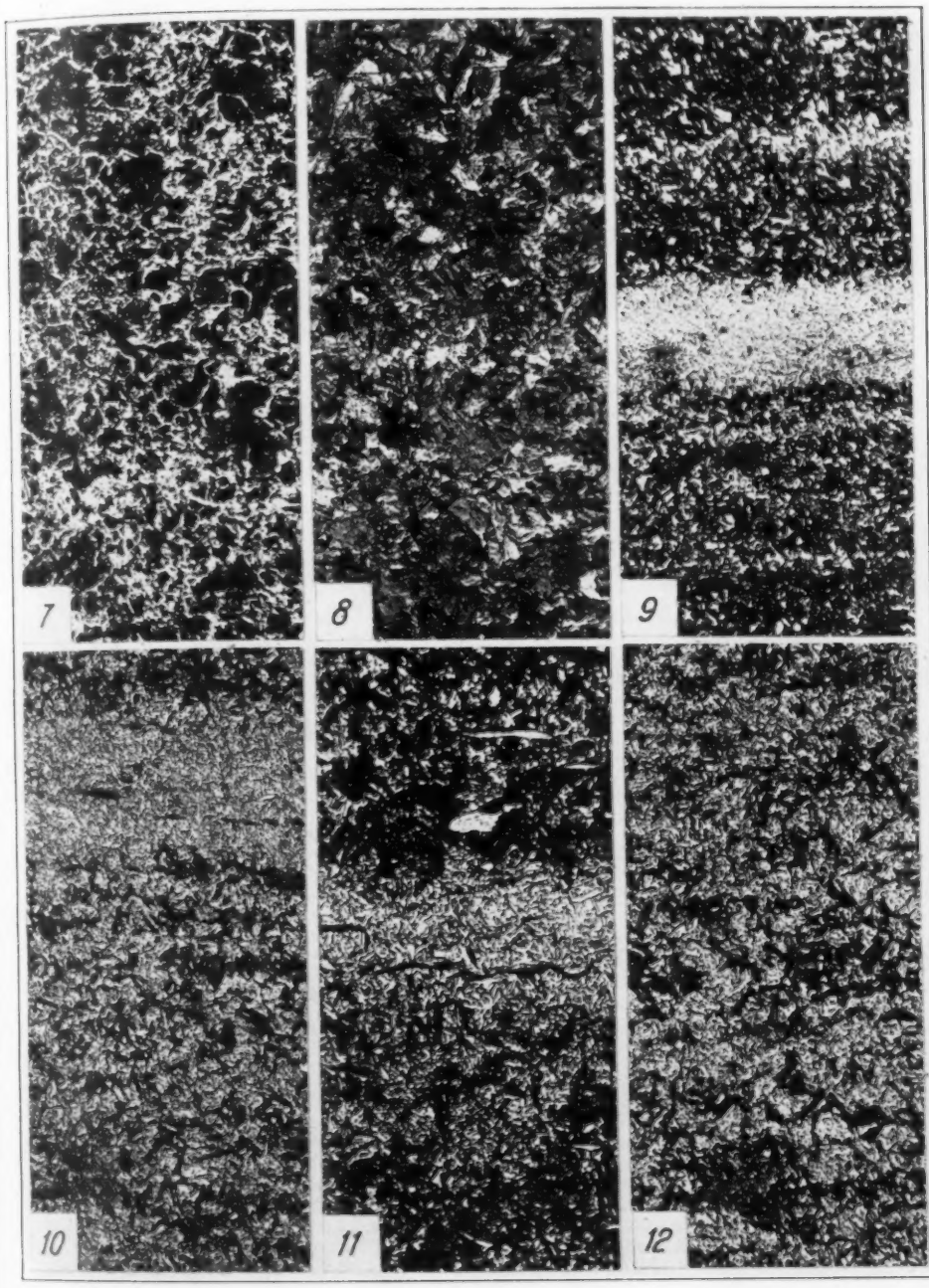


Fig. 7—Single Normalize at 800 Degrees Cent. Structure Shown in Fig. 6 was Identical with Above Structure Before the Second Normalizing. Etchant Picric-Nitric Solution. × 100.

Fig. 8—1.8 Per Cent Manganese Steel, Hot-Rolled. 5 Per Cent Nitric Etchant. × 100.

Fig. 9—Specimen M-2. 1.8 Per Cent Manganese Steel Annealed 30 Minutes at 750 Degrees Cent., Air-Cooled. Etchant 5 Per Cent Nitric Acid in Alcohol. × 100.

Fig. 10—Specimen M-4. 1.8 Per Cent Manganese Steel Annealed at 800 Degrees Cent. for 30 Minutes, Air-Cooled. Etchant Same as Fig. 9. × 100.

Fig. 11—Specimen M-5. 2-Hour Anneal at 800 Degrees Cent. × 200.

Fig. 12—Specimen M-6. 1.8 Per Cent Manganese Steel Annealed 30 Minutes at 850 Degrees Cent. and Air-Cooled. Etchant 5 Per Cent Nitric Acid in Alcohol. × 100.

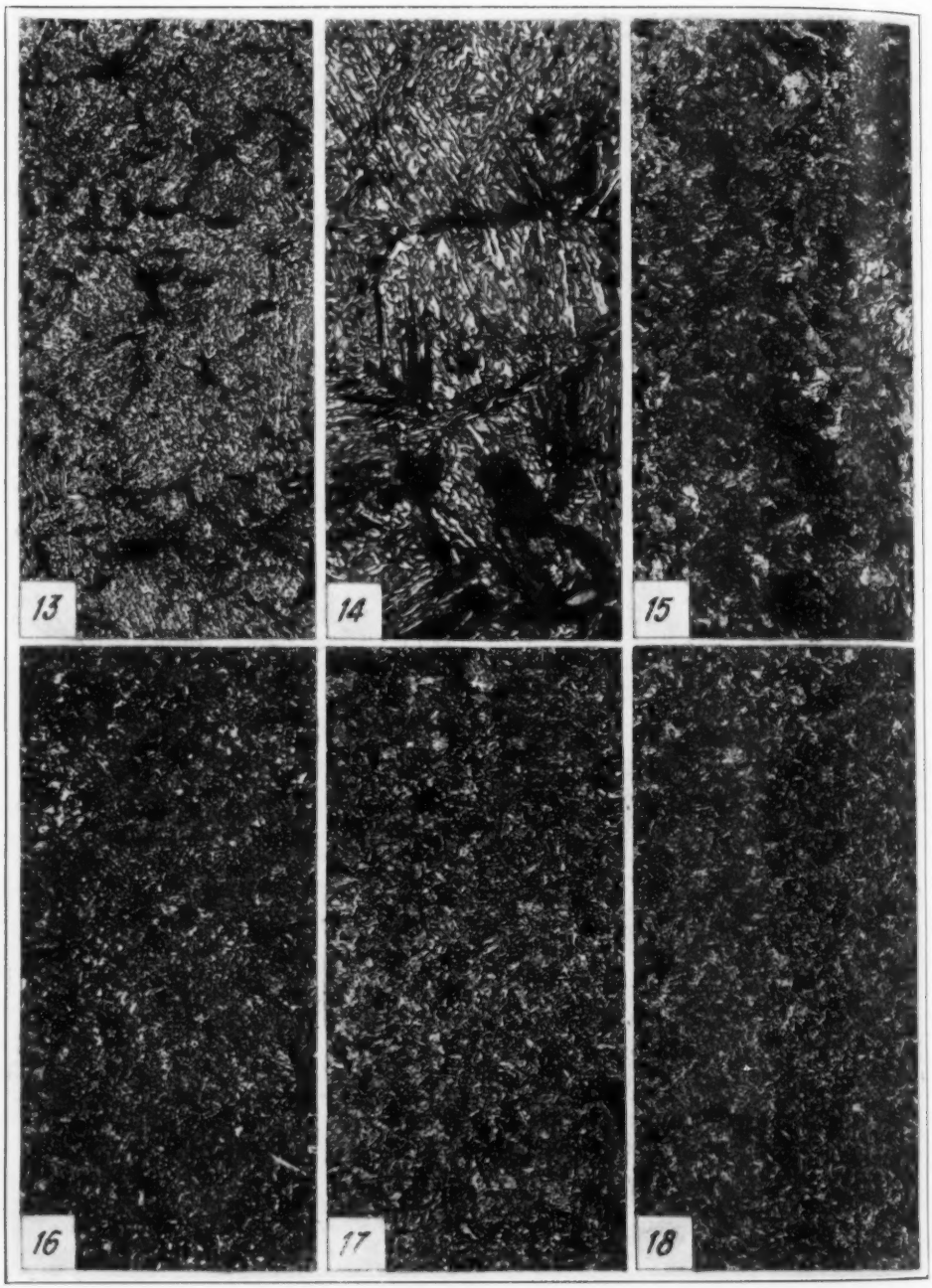


Fig. 13—Specimen M-7. 1.8 Per Cent Manganese Steel Annealed at 1000 Degrees Cent., Air-Cooled. Etchant 5 Per Cent Nitric Acid in Alcohol. × 100.

Fig. 14—Specimen M-7. Same as Sample Fig. 13 at Higher Magnification. Etchant Same as Fig. 13. × 500.

Fig. 15—Specimen AQ-15. Annealed 30 Minutes at 800 Degrees Cent., Cooled in the Open Furnace. Etchant 5 Per Cent Nitric Acid in Alcohol. × 100.

Fig. 16—Specimen AQ-11. Annealed 30 Minutes at 800 Degrees Cent., Air-Cooled—"Normalized." Etchant Same as Fig. 15. × 100.

Fig. 17—Specimen AQ-13. Annealed 30 Minutes at 800 Degrees Cent., Air-Cooled. Tempered at 450 Degrees Cent. 30 Minutes. 5 Per Cent Nitric Acid Etchant. × 100.

Fig. 18—Specimen AQ-17. Annealed 30 Minutes at 800 Degrees Cent., Air-Cooled. Tempered at 625 Degrees Cent., for 30 Minutes. Etchant Same as Fig. 17. × 100.

Table X
Computed Tensile Values after Normalizing

Specimen No.	Rockwell "C" Hardness	Brinell Hardness	Tensile Strength Pounds Per Square Inch	Heat Treatment
M3	28.8	280	137,000	Hot rolled.
M2	42.0	431	211,000	Air cooled after 30 min. at 750°C.
M4	51.0	510	250,000	Air cooled after 30 min. at 800°C.
M6	52.0	521	255,000	Air cooled after 30 min. at 850°C.
M7	61.5	650	318,000	Air cooled after 30 min. at 1000°C.

treatment nomenclature. In small sections the steel has very marked air-hardening properties. Manifestly, therefore, little useful information could be gained by obtaining a complete series of physical tests to demonstrate the effect of "normalizing" on the properties of this steel. It was considered, however, that the effects of certain heat treatments on the Izod impact values of the steel might be of interest.

Effects of Certain Heat Treatments on the Izod Impact Values of the 1.8 Per Cent Manganese 0.6 Per Cent Carbon Steel

Four different heat treatments were given to pairs of Izod impact specimens.

1. Anneal for 30 minutes at 800 degrees Cent. (1470 degrees Fahr.) and air-cooled. This may be regarded as the optimum condition for a single normalizing treatment.
2. Anneal for 30 minutes at 800 degrees Cent. and cooled in an open furnace from the temperature of anneal. This approximates to a medium slow cool.
3. Annealed 30 minutes at 800 degrees and air-cooled, followed by a temper at 425 degrees Cent. (800 degrees Fahr.) for 30 minutes.
4. Annealed 30 minutes at 800 degrees Cent. and air-cooled, followed by a 30-minute temper at 625 degrees Cent. (1160 degrees Fahr.).

Rockwell hardness values were taken on the specimen in each case and the Brinell hardness and tensile strength computed as in the previous series of tests. The results are recorded in Table XI.

The temperature of 800 degrees Cent. (1470 degrees Fahr.) was selected because this would be the most favorable treatment

Table XI

Computed Tensile Values and Actual Izod Impact Values after Normalizing and Tempering

Specimen No.	Izod Impact Value Foot-pounds	Rockwell "C" Hardness	Brinell Hardness	Tensile Strength Pounds Per Square Inch	Thermal Treatment
AQ11	2.0	36.5	352	172,000	Annealed 30 minutes at 800°C and air cooled
AQ12	2.0	35.9	346	169,000	
AQ15	2.4	27.1	268	131,000	Annealed 30 minutes at 800°C and furnace cooled
AQ16	2.9	26.6	262	129,000	
AQ13	5.9	33.7	323	158,000	Annealed 30 minutes at 800°C, air cooled, and tempered at 425°C
AQ14	5.2	34.0	326	160,000	
AQ17	8.5	26.0	259	127,000	Annealed 30 minutes at 800°C, air cooled, and tempered at 625°C
AQ18	7.9	27.0	267	130,000	
AQ	1.4	28.1	275	135,000	As received, in the hot rolled condition

if the steel could show improved physical properties after a normalizing treatment.

It was pointed out that from a consideration of the results of microscopic examination a normalizing treatment could not be expected to materially improve the properties. This is demonstrated by the Izod values obtained from such treatment and also from the computed tensile strength. It is also shown that a temper as high as 625 degrees Cent. (1160 degrees Fahr.) following air hardening, brings the tensile down to about 130,000 pounds per square inch, but raises the Izod to a little over 8 foot-pounds. Presumably a higher tempering temperature adjusted to give 110,000 pounds per square inch tensile, the value required of this particular steel, would further appreciably increase the Izod value.

The metallographic features of the last series of tests are presented in Figs. 15 and 18 inclusive. The homogeneous character of the steel should be observed from these illustrations. There is a complete absence of the banding found in the earlier experiments (Figs. 8 to 14). Both sets of samples were cut from the same piece of steel but at different locations. This indicates the lack of homogeneity over different sections of the steel, and also the marked segregation effects to which a steel of the given composition is subject. These observations indicate the need for carefully studying the analysis of these medium manganese steels before adopting for some particular service.

DISCUSSION

Written Discussion: By A. Oram Fulton, president, Wheelock, Lovejoy and Co., Cambridge, Mass.

The author has contributed some interesting data on the effect of the double normalizing treatment on medium manganese steels, and brings out emphatically the remarkable increase in ductility and resistance to impact when the double treatment is used. Of course, all of these steels are much better when the regular heat treating operation can be used, that is, a quench and draw, but where mechanical handling makes this impracticable the double normalizing treatment does undoubtedly materially improve physical properties. This is, of course, analogous to the effect obtained in regular heat treating operations when using a double quench or a double tempering operation, the second temperature in each case being the lower one.

There is one interesting phase to this matter which the author did not touch upon, and that is the effect of the double normalizing on the machinability of the steel. While this may not be of practical importance in the case of the pipe to which the author refers, it would be highly important to the manufacturer of small parts using bar steel. Probably investigation of this phase would show that double normalizing does improve the machining. Medium manganese steels have to a certain extent air hardening properties, and the second heating and cooling at lower temperature would tend to relieve any hardness induced by the first operation. This machinability would, undoubtedly, vary depending upon the temperatures used and the rate of cooling. This would determine the proportion of sorbite and pearlite in the resulting sorbito-pearlitic structure, just as in the case of the same steels when quenched and tempered, the quenching and drawing temperatures determine the relation of the sorbite and troostite, resulting in these steels with ideal heat treatment.

The author's excellent paper and the conclusions drawn simply again emphasize the need of careful selection not only of the proper analysis of these medium manganese steels for each job under consideration, but even more important the careful and proper heat treatment to be applied to each of the analyses selected.

Written Discussion: By Norman E. Woldman, metallurgical engineer, Material and Process Engineering Department, Westinghouse Electric and Manufacturing Co., East Pittsburgh.

This paper should be of great value to manufacturers of steel products using pearlitic-manganese steels. Dr. Austin has ably brought forth the vital fact that pearlitic-manganese steels must be properly conditioned to obtain maximum service and life from the manufactured product, especially where the fabricated product is subjected to shock and impact in service.

In the manufacture of gears and pinions some tendency in the past had been to use 1.5 per cent manganese steels containing from 0.35 to 0.50 per cent carbon. These gears and pinions were either annealed, normalized, oil-quenched or water-quenched. Pinions were made from either hot-rolled bars, forged bars or upset forged blanks. Gears and also very large pinions were made from either die-rolled or cast blanks. The proper conditioning of these steels was sadly neglected. Nonhardened gears and pinions were merely annealed

at a high temperature or released in the green state for finish machining. Such gearing would most assuredly fail after a short period in service, and would disclose on microscopic examination of the metal at or adjacent to the fracture a coarse structure, ferrite banding, probably ferrite segregation and frequently minute cracks. Due to the low impact value, the teeth would fracture out at the root, the corners of the teeth would chip off if full bearing was not obtained, and worst of all the pinion would split open usually at the top and corner of the keyway.

The greatest grief was usually obtained in hardened 1.5 per cent manganese steels. Many steel fabricators believed that if the manganese steel articles, such as gears, pinions and the like, were to be hardened by oil or water quenching, it was not necessary to give the articles a preliminary annealing or normalizing treatment. The result was a steel of high strength and hardness, but of low ductility and impact values with subsequent decreased toughness. Microscopic examination of such heat treated products would show countless internal ruptures and fine cracks, traces of ingotism and possibly coarse dendrites. After quenching and tempering there would be observed microscopic quenching cracks at the end of the teeth, these cracks running approximately at a 30-degree angle from the tooth top to the tooth root. Such heat treated pinions would shortly crack through the keyway after a short service. Failures were not due to defective steel or defective hardening heat treatment, but rather due to the steel not being properly conditioned before heat treatment.

The better gear manufacturers today specify that unhardened manganese steel gears and pinions must be either thoroughly annealed and followed by a normalizing operation, or must be doubly normalized, or must be normalized and followed by a low anneal or strain relieving draw to obtain the desired strength with the highest ductility and good impact values. For hardened manganese steel gears and pinions, whether oil-quenched or water-quenched, they specify that the gear and pinion blanks must be properly conditioned by a normalizing operation before machining so as to obtain uniform structure and subsequent uniform physical properties after hardening. Such heat treated manganese steel gears and pinions would then have the maximum shock and impact resistance in the as-hardened condition.

Pearlitic manganese steels are very tough steels, but rather treacherous in hardening heat treatments if said steels are not properly conditioned prior to the hardening heat treatment.

Heat treaters should carefully note, as Dr. Austin has pointed out, that the temperature range for properly normalizing pearlitic manganese steels is smaller than the temperature range for normalizing plain carbon steels.

Written Discussion: By R. H. Frank, metallurgist, The Bonney-Floyd Co., Columbus, Ohio.

The writer wishes to compliment the author for his excellent paper on normalizing medium manganese steels and especially on the results obtained by double normalizing. All of Mr. Austin's work was conducted on rolled steels, and I think it would be interesting to know if he has conducted any research in the "as-cast" condition. We market a steel of slightly different com-

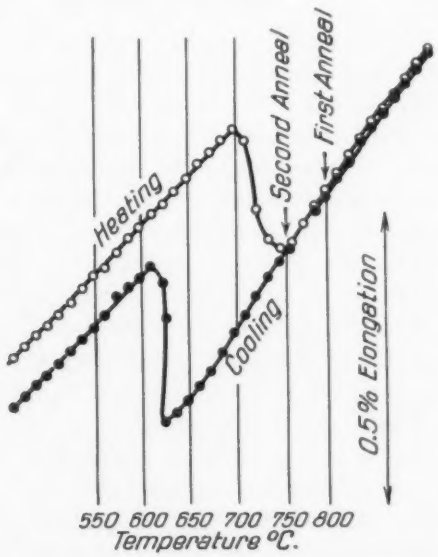
position, namely, C-0.30; Mn-1.25 and Mo-0.20 upon which similar experiments have been conducted. Cast bars one inch square were normalized from 1675 degrees Fahr. and the double normalized bars were given an additional air quench from 1525 degrees Fahr. while all bars were tempered at 1100 degrees Fahr. for one hour with the following results which are averages of a number of tests.

	Elongation in 2 Inches	Reduction of Area	Yield Point	Ultimate Strength
Single normalize	22.5	52.8	74,600	101,300
Double normalize	25.0	60.0	73,000	99,500

A considerable increase in ductility was obtained at the expense of a slight decrease in strength which corresponds favorably with Dr. Austin's results except that he obtained an increase in yield point results. The writer would like to ask Dr. Austin if he considers this difference due to the composition or the fact that his samples were started from the rolled condition.

Written Discussion: By M. Gensamer, Bureau of metallurgical research, Carnegie Institute of Technology, Pittsburgh.

I have had the opportunity to carry out dilatometric studies of the same steel used by Dr. Austin. My purpose is to correlate this dilatometric analysis with Dr. Austin's experimentally determined heat treatments, and to show



what great assistance can be rendered by the dilatometer in an investigation of this kind. The dilatometer used is the simple one described before this society at last year's meetings.*

The accompanying illustration represents a typical heating and cooling cycle on Dr. Austin's steel. The length of a 1-inch specimen is plotted against its temperature. The contraction in the neighborhood of 700 degrees

*F. M. Walters, Jr., and M. Gensamer, "Alloys of Iron, Manganese and Carbon—Part IV," TRANSACTIONS, American Society for Steel Treating, Vol. 19, May, 1932, p. 608.

Cent. (1290 degrees Fahr.) is the alpha to gamma transformation on heating, and includes both the eutectoid transformation (which is not a constant temperature change because we are dealing with a ternary alloy) and the change involving the excess constituent, free ferrite. The expansion around 620 degrees Cent. (1150 degrees Fahr.) is the reverse reaction. Only the significant parts of the curves have been shown: at temperatures below those indicated in the graphical illustration, the slope of both heating and cooling curves is the same and is typical of alpha iron, with no indication of any reaction at lower temperatures; except for the first heating curve for every specimen, which possesses a greater slope. Heating or cooling at a faster or slower rate (excluding quenching) produce no significant changes in the curves. Extremely rapid cooling lowers the temperature of transformation, but cooling in still air does not lower the temperature more than 10 to 20 degrees Cent. Cooling from a lower temperature than indicated, as long as it is above the transformation range, gives the same curves.

Dr. Krivobok has recently obtained nearly identical results with a steel of the same class, but of different composition, and he also has given me a sample which I have studied in this way. Both Dr. Austin's and Dr. Krivobok's steels gave results so nearly identical that the illustration represents both.

The story told by Dr. Austin's experiments supplemented by the dilatometer is as follows. It is necessary to exceed 750 degrees Cent. (1380 degrees Fahr.) to complete the alpha to gamma transformation, but on the first anneal Dr. Austin's work shows that 775 to 800 degrees Cent. (1425 to 1470 degrees Fahr.) is necessary. Otherwise it is impossible to eliminate carbon segregation, shown by the large ferrite areas at the grain boundaries in the "as-rolled" condition. No evidence is given by the dilatometer of this diffusion process, so the temperature necessary to achieve homogeneity must be determined by a series of experiments involving examination under the microscope. This anneal at 800 degrees Cent. (1470 degrees Fahr.) treatment is not compatible with the refined grain necessary for best physical properties. Dr. Austin has shown that in this steel, as in general, the grain size increases as the annealing temperature increases. Hence a second anneal is necessary, this time to the temperature of completion of the alpha to gamma transformation, and no higher. The gamma grains formed in this transformation are initially small, and holding the temperature down limits the size to which they can grow. This double treatment produces a fine-grained structure which is free from large ferrite areas and hence microscopically more homogeneous.

The superiority of the dilatometric method over the thermal determination of critical points is demonstrated by the exactness with which the temperature of completion of the transformation can be ascertained. Whereas, Dr. Austin was compelled to experiment with various annealing temperatures, dilatometric analysis tells at once that 750 degrees Cent. (1380 degrees Fahr.) is the best final annealing temperature, and indicates that for preliminary annealing, temperatures below 775 degrees Cent. (1425 degrees Fahr.) or so need not be investigated.

Written Discussion: By Jerome Strauss, chief research engineer, Vanadium Corporation of America, Bridgeville, Pa.

Dr. Austin has selected a steel of considerable commercial value and importance, and rightly pointed out its shortcomings, along with one method of overcoming some of them. Those of especial importance are the tendency of these steels toward coarse and nonuniform grain size, the sensitiveness of this grain size to temperature and the ill influence of these characteristics upon impact value when the steel is subjected to treatment other than quenching and tempering.

The heat treatment proposed, similar to that employed in improving the less desirable properties of steel castings found in the "as-cast" condition, is effective. This importance of the normalizing treatment often is overlooked, but is, in many cases, the only economical means of securing the desired mechanical properties in parts of large size and small section, or of very irregular nature.

However, a double treatment such as that recommended is not the only way out of the difficulty. A modified composition combined with a single normalizing has in one instance not only accomplished the same purpose, but secured further improvement in tension test values. The modified composition is:

C	Mn	Cr	V
0.40	1.20	0.35	0.10

giving the following properties:

Tests of Mn-Cr-V Steel

1-inch Round—Normalized 1600 Degrees Fahr.

Heat No.	Bar No.	Yield Point Pounds per Square Inch	Tens. Strength Pounds per Square Inch	Elongation PerCent in 2 Inches	Reduction of Area	Izod ft.-lb.
1	1	80,050	118,300	25.5	61.6	41.5
1	2	80,400	118,250	25.0	61.3	44.3
2	1	86,450	117,050	23.0	52.5	55.5
2	2	82,400	118,100	23.0	54.4	52.8
1	3*	75,550	116,750	22.5	56.0	34.0

*2-inch Round—Normalized from 1625 Degrees Fahr.

Attention is directed to the fact that these data are from larger sections, and that nevertheless the yield point, reduction of area, and Izod value are higher than in the plain manganese steel. Furthermore, in this composition, there is much less sensitivity to the influence of temperature of working and treatment.

E. E. THUM[1]: I believe it would be a mistake if those present would assume from Dr. Austin's paper that the medium manganese steels are dangerous to use unless properly heat treated, because of an inherent brittleness.

I would like to call your attention to the fact that raising the manganese is one of the favorite ways of improving the tensile properties of the ordinary structural steels, and a considerable quantity of such strong steels, probably equal in tonnage to the tonnage of the medium manganese steels that are heat treated, is rolled into plates and shapes for extremely large structures. An important instance is the 1675-foot Kill Van Kull Arch which spans the neck of

[1]Editor, *Metal Progress*, American Society for Steel Treating, Cleveland.

water between Bayonne, N. J., and Staten Island, N. Y. The principal arch chords were built with one of these medium manganese steels and the plates and shapes were used in their as-rolled condition.

From information kindly forwarded me by O. H. Ammann, chief engineer of bridges, Port of New York Authority (the builder of this bridge), I quote the following purchase specification:

Carbon	0.40 per cent maximum
Manganese	1.80 per cent maximum
Ultimate tensile strength	90,000 pounds per square inch minimum
Yield point	55,000 pounds per square inch minimum
Reduction of area	30 per cent minimum
Elongation in 2 inches	16 per cent minimum

Half-scale models of the large compression members on this bridge were made of carbon structural steel, "silicon structural steel," and the above medium manganese steel and tested in compression in the 10-million pound machine at the Bureau of Standards. The proportional limit of the columns, as determined from the stress-strain curve, was 17,500, 21,000, and 23,000 pounds per square inch for the above three steels, while the stress at failure by buckling was 33,500, 53,000, and 62,000 respectively. It is apparent that the engineers on this structure were justified in loading the medium manganese steel proportionately.

I would also call your attention to the fact that a very large tonnage of medium manganese steel, with considerably more carbon than the samples analyzed by Dr. Austin, is being rolled every year into railroad rails, and used in the as-rolled condition, without separate heat treatment.

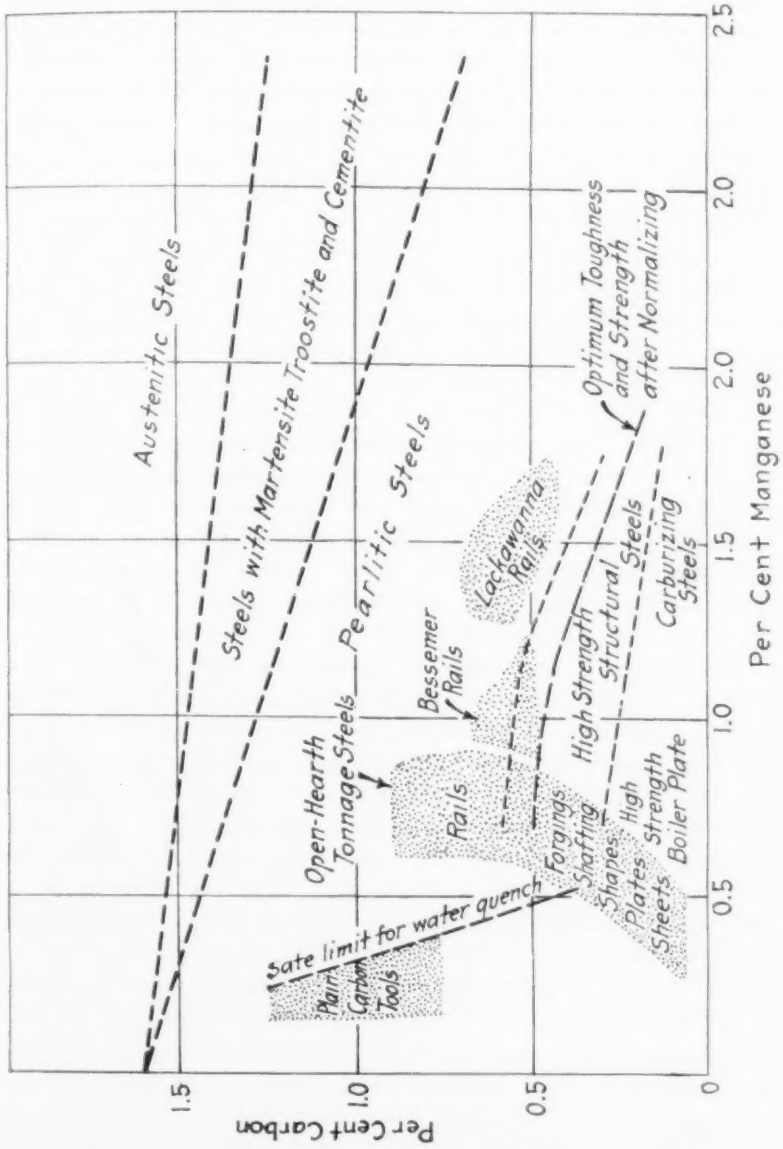
For instance, in the year 1929 the tonnage was about 150,000 tons. This rail is the standard for the Lackawanna system, using 105 to 130-pound sections; no other rails have been bought by it for six or seven years. A big percentage (perhaps 40 per cent) of the rails bought recently by the New York Central lines are of the same analysis: C 0.54 to 0.67, and Mn 1.30 to 1.50.

As will be observed, these rails are much higher in carbon and approximately the same in manganese; if anything, they would be supposed to have lower impact values than the ones recorded by Dr. Austin, namely, 4.5 foot-pound Izod.

Rails are ordinarily tested full size under a drop hammer. Some Izod impact tests cut from this medium manganese steel rail averaged 4.3 foot-pound, which is in the same range as Dr. Austin's metal. While this is low, it is apparently sufficient for the very severe service of American main-line traffic. In fact, this figure is about twice as tough as the regular carbon steel rail; comparable tests for it average 2.2 foot-pound Izod.

Since these rails, laid in the track exactly as they are cooled on the hot bed, have been very satisfactory, it is certain that a medium manganese pearlitic steel, even in fairly large sections such as 130-pound rails, is not too brittle as-rolled. Stated in another way, even though the Izod value of such a rail would be less than 5 foot-pound, the steel is sufficiently tough to withstand the very severe punishment it gets in the main line tracks of American railroads.

The medium manganese rail has been adopted because of its superior resistance to wear (0.0018 square inch of section per million tons traffic as compared to 0.0045 square inch for standard open-hearth rails). The experience with it is hardly long enough to indicate that it will cure the transverse fissure problem, but there have been no disquieting reports in the six or eight



Relation Between Carbon and Manganese in Tonnage Steels.

years in which this heavy alloy rail has been in use. Transverse fissures were practically nonexistent in high manganese 80-pound rails rolled in the 1890's at the old Scranton mill of the Lackawanna Iron & Coal Co. Therefore we must conclude that it is not a brittle rail, as-rolled.

The difficulty which the railroad people have is in properly adjusting the relationship between carbon and manganese. If the manganese gets a little high, then the carbon must be reduced, or vice versa.

If both of the elements are on the high side of the analysis at the same time, they are liable to get some broken rails in service, and ordinarily a microscopic investigation will show small areas of martensite in the head of these rails. On the other hand, if the carbon and manganese are a little low, then they get trouble due to soft rails which flow under traffic.

I have no doubt but that a rail steel, even though the microstructure is predominantly pearlite, and has no excess constituent in it, would have a vastly improved Izod impact test if it were heat treated in the way suggested by Dr. Austin, but I would emphasize that the pearlitic manganese steel, even in its condition as-rolled, and even though it does have low impact value, is a very useful steel for severe service. This might be interpreted as a criticism of the correlation of impact testing to service; if you wish to interpret my remarks in that light you are welcome to do so.

The accompanying diagram shows the relationship between carbon and manganese in American tonnage steels. It was first published in *Iron Age*, March 21, 1929, and later in a paper on "The New Manganese Alloy Steels" read before the American Society for Testing Materials in 1930. It shows at a glance how carbon must be reduced as manganese is increased. Similar conditions exist between the two elements in two other important classes of heat treated alloys. If a line is drawn from C 0.3, Mn 1.0, to C 0.2, Mn 2.3, high strength castings occupy the field below it. Above that line and below another drawn from C 0.65, Mn 1.0, to C 0.40, Mn 2.0 will be found springs, heat treated forgings, and gun barrels.

H. J. FRENCH[2]: I have some questions I should like to ask. During the last few years it has been reported that some of the intermediate manganese steels have shown temper brittleness, and I should like to ask whether Dr. Austin, in his impact studies, has ever encountered any effects of this sort.

Then, too, I notice that the cracks in the photomicrographs were at areas bounded by martensitic or pseudo-martensitic structures.

I am unable to evaluate the dilatometric records shown by Mr. Gensamer, who discussed the paper, but the volume changes looked rather large. I would ask whether Dr. Austin has any data showing the relation between these volume changes and the cracking shown in his photomicrographs.

C. H. HERTY[3]: When I first read Dr. Austin's paper, my mind immediately went back to the first high manganese rail that was made in a steel plant that I started in. I remember we very carefully figured out the tensile strength from the existing data and made the heat according to a certain carbon and manganese specification. The rails rolled beautifully.

When the rails went to the drop test, you would have thought the war had started all over again; they boomed like big guns. The result was that the

[2]In charge alloy steel and iron development, The International Nickel Co., New York City.

[3]Director of Research, mining and metallurgical advisory boards, Carnegie Institute of Technology, Pittsburgh.

specifications had to be changed to get away from this brittleness. I think Dr. Austin's paper is very pertinent in this respect.

They are finding in industry now that the best results that can be obtained from these high manganese rails are in a semi-heat treated condition. I know of two plants that are normalizing these steels, somewhat the same type of thing that Dr. Austin is doing.

I think work on this particular range of carbon and manganese contents is extremely important from the standpoint of utility and safety.

I would like to say this about those steels in connection with some work we have been doing on impact testing. We have started out on impact testing with this in mind. There must be some reason why two heats of a given analysis, say, 0.40 carbon and 0.70 manganese, should give an impact of 12 foot-pounds and 22 foot-pounds when, as far as we know, they are made in the same way.

We have found this (which checks with Dr. Austin's work) that given an identical heat treatment one steel would have a ferrite content of 20 per cent and another steel of the same analysis would have a ferrite content of 45 per cent, and the impact values that are obtained from the two steels are proportional to the amount of ferrite and the composition of the ferrite. That is a fundamental concept. In other words, the amount of ferrite controls the ductility effects that you get in impact testing, and the amount of ferrite varies tremendously in steels of the same composition. We have taken, for example, two steels of the same composition and found that in the annealed state both steels contain 45 per cent ferrite. In the normalized state, from a half inch to a 1-inch bar, one steel may contain 7 per cent of ferrite and the other 25 per cent ferrite. The rate at which these steels recrystallize, the rate at which they form ferrite from austenite, is important from the standpoint of using these steels and the performance they give in service.

I am sorry that I did not have access to the original photomicrographs of Dr. Austin. We might have given some concrete evidence on how our work checks with Dr. Austin's. However, by looking at the micrographs it is evident that Dr. Austin has increased the amount of ferrite and thus raised the impact value, and in certain ranges of composition, particularly in high manganese steels, that is extremely important. The impact value can be raised if you can raise the amount of ferrite in that steel.

I would like to congratulate Dr. Austin on this paper. I think he has done a very great service to anybody who is interested in the impact strength of that type of steel and in other types of steel.

Author's Closure

Mr. Fulton suggests that all these steels are much better after a quench and draw, but that otherwise a double normalizing gives material improvement. I feel that this is true when the carbon and manganese contents are permitted to reach the values given in the appendix to the paper, but when the carbon is not above 0.4 per cent and the manganese say 1.4 per cent, a double normalizing puts the steel in the condition providing optimum physical properties.

Probably the machinability was improved by the double treatment. No comments were made by the engineer who prepared the test samples, so we can presume that the treatment did not increase the machining difficulties. Any difference in machinability would be due to the production of a fine grain structure, rather than to any relief of internal stresses. An effort at close correlation of Brinell hardness values with heat treatment was not successful, as I mentioned in the paper. In any case, it is unwise to assume a close relationship between hardness and machinability.

Mr. Frank asks for data on the as-cast steel. The only steel available was obtained from tubular products. It is not quite clear from Mr. Frank's comments how the test bar in his own work was double normalized. The initial treatment at 915 degrees Cent. (1680 degress Fahr.) may be assumed to be a homogenizing treatment. If this is the case, then a higher temperature would be more desirable, followed by cooling through the critical range. As part of a normalizing treatment, 915 degrees Cent. is regarded as too high a temperature. This tends to lead to the development of a coarse structure with separation of ferrite in relatively large particles, leaving little excess ferrite in the transforming eutectoid. It is considered that this probably permits the less ductile pure eutectoid aggregates to impose their more brittle characteristic properties on the steel. Large ferrite areas also lead to a decrease in the strength, just as in the case of ordinary carbon steels. I think it would have been of great interest if Izod values had been available on the steel discussed by Mr. Frank. I believe that the test samples would have shown rather low impact values.

Dr. Woldman's contribution is of particular interest by virtue of the manner in which he illustrates the importance of giving greater attention to the heat treatment of pearlitic steel manufactured products; in some cases it appears that "some attention" to heat treatment constitutes an advance. I would like to add, however, that in many instances the total manganese-carbon content is allowed to reach too high a figure. In general, the higher the manganese analysis the less the carbon which can be permitted to remain in the alloy. I have cited an extreme case in the appendix.

Undoubtedly the application of the steel is of considerable importance in considering just what composition may be permitted. Relative to that point I feel that I agree with Mr. Strauss that a modification of the steel by the addition of another element is really the answer to the problem of overcoming the carefully controlled treatment that seems to be necessary for these steels having a carbon plus manganese content on the high side. At present there is not sufficient information available to state just where the danger line appears. As I stated, it seems that the percentages I gave for manganese and carbon are safe for fabricated products (1.4 per cent manganese and 0.4 per cent carbon). On the other hand, when we reach 1.8 per cent manganese with 0.6 per cent carbon, we seem to be definitely in the danger zone.

I very much appreciate the contribution from a member of the Carnegie Metallurgical Bureau where so much noteworthy research has been conducted on the iron-manganese alloys.

I was able to supply Mr. Gensamer with a sample furnished by Dr. Speller

of the identical steel used in the experiments which I have described to you, and Mr. Gensamer's dilatometric observations confirm that any change in temperature from which the steel is cooled has no effect on the temperature of transformation. His observation relates essentially to the use of the dilatometer as a substitute for thermal analysis.

The work described in my paper was completed some three years ago, and it is only more recently that the advantages of dilatometric analysis have been emphasized by Mr. Gensamer and his colleague.

An important point made by Mr. Gensamer is that relating to the amount of free ferrite in the heat treated steel. On page 445 of the paper it is stated that the annealing was conducted so that the aggregation of free ferrite was restricted to a minimum in order to give optimum physical properties. I think Mr. Gensamer states the theory concisely by use of the phrase "microscopically more homogeneous".

I have already made reference to the remarks made by Mr. Strauss, and I believe that the modification of these medium manganese steels by the addition of small amounts of one or more elements would provide a fruitful field for research. The mechanical properties he cites for a manganese-chromium-vanadium steel are of considerable importance.

The contribution by Mr. Thum is welcomed and appreciated. I refer to Mr. Thum's contribution to our knowledge on these steels on the first page of the present paper, and I appreciate the fact that the "Lackawanna rails" area given in his diagram (Fig. 1) in the paper cited lies in a manganese-carbon composition region very close to what I have termed the danger zone.

It should be clearly noted, however, that the purpose of my paper was to analyze the effects of heat treatment on the properties of 1.4 to 1.6 per cent manganese and 0.4 per cent carbon steel and to demonstrate the superiority of such properties over those found in the rolled steel. It was certainly not my intention to have any user infer that these steels "are dangerous to use unless properly heat treated", for these same steels are used with advantage every day in fabricated tubular products in the as-rolled condition. Nevertheless, it is important to note the marked increase in the numerical value of the properties which result from proper heat treatment.

On the other hand, in the appendix to the paper I have attempted to give warning to the serious effects on ductility which may be expected when the carbon reaches about 0.65 per cent with 1.8 per cent manganese. The application of such a steel to any commercial purpose in the as-rolled state would seem to be undesirable. Mr. Thum indicates that the railroad people have difficulty in properly adjusting the relationship between carbon and manganese, and that if both elements are on the high side of the analysis at the same time, they are liable to get some rails broken in service. It would be a definite advance in our knowledge of these alloys if "safe limits" could be more clearly defined.

With reference to Mr. French's question on temper brittleness, I must admit that I have no data on this property. The nature of the investigation would not reveal the presence of temper brittleness even if the steels were susceptible.

Neither do I have data to permit correlation between dilation and cracking as shown on the photomicrographs. Experience with these steels, however, indicates that what I have termed the pseudo martensitic structure is practically completely devoid of ductility, and it is reasonable to assume that the stresses set up by differential dilation result in the formation of incipient cracks.

Dr. Herty brings the discussion back to rail steels and his experience substantiates the comments in the paper with respect to the danger lurking in the utilization of the steels without careful control of manganese plus carbon content. This statement holds despite the lack of respect with which anyone may regard any form of impact test.

I consider that Dr. Herty raises an important point when speaking of the amount of free ferrite separating in the steel, but I am not quite sure whether I completely agree with his analysis of the problem. He states that the impact value is greater the greater the amount of ferrite which is allowed to separate from the gamma solid solution prior to the eutectoid transformation. I agree completely with this statement, but I must add that the state of aggregation of this separated free ferrite is of paramount importance.

In his 0.4 per cent carbon 0.7 per cent manganese steels Dr. Herty was able to estimate the amount of free ferrite by planimetric methods under the microscope at low magnifications. During my own research some three years ago I attempted a similar analysis, but even at high magnifications was unable to attain much success, due to the fine structure of the higher manganese alloy. However, we appeared to obtain fairly conclusive evidence that the improvement in the impact values depended on:—

1. The maximum separation of free ferrite before the eutectoid transformation took place.
2. The least possible aggregation of these separated ferrite particles.

When the free ferrite particles were permitted to aggregate to form areas of such size that they could be readily discerned under the microscope, then there was a fall in impact strength. As previously mentioned, the state "microscopically homogeneous" appeared to be most desirable.

Thus I am in agreement with Dr. Herty on the importance of maximum ferrite separation, but I am uncertain as to how to interpret his view on "ferrite aggregation". Furthermore, there may be important differences in the effect of this latter factor on steels of such different manganese content.

Finally I should like to conclude by expressing my thanks and appreciation to those who contributed to the discussion of this paper.

TRANSFORMATION IN THE CARBIDE PHASE DURING GRAPHITIZATION

By H. A. Schwartz, Kent R. Van Horn and C. H. Junge

Abstract

New data regarding the cementite phase in the iron-carbon system are presented. It is shown that cementite during the process of graphitization is not of constant composition, hence is Fe_3C only if certain time-temperature conditions have been realized.

The chemical and crystallographic characteristics of this new variant of iron carbide are recorded.

The sequence of changes in the cementite phase during graphitization are worked out.

It is suggested that the term cementite should be applied to any phase of this space lattice, the term iron carbide being reserved for such a phase when of the composition Fe_3C.

Introduction

TWO of the authors,[1] with Johnson, have suggested that cementite is not always of the composition Fe_3C. Bates and Lawson,[2] with one of the authors have shown that the composition may vary in either direction from the theoretical, a higher carbon content being perhaps associated with graphitization. Schüz and Stotz,[3] show that cementite in white iron heated to graphitizing temperature decreases in amount for an appreciable time before temper carbon forms and assign this to the time required to saturate austenite, erroneously in our opinion.

It is the purpose of the present paper to elucidate further the changes occurring in cementite during the process of graphite forma-

[1]H. A. Schwartz, H. H. Johnson and C. H. Junge, "Graphitization of Prequenched White Cast Iron," Transactions, American Society for Steel Treating, Vol. 17, 1930, p. 383.

[2]A. A. Bates and D. E. Lawson, "Metastable Equilibrium in Hypereutectoid Iron-Carbon Alloys," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 659.

[3]Schüz and Stotz, "Der Tempergusz, Springer," 1930, p. 56 et seq. and Fig. 42.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, who are members of the society, H. A. Schwartz is manager of research and C. H. Junge is a member of the research staff, National Malleable and Steel Castings Co., and Kent R. Van Horn is research metallurgist, Aluminum Co. of America, Cleveland. Manuscript received January 22, 1932.

tion. It is recognized that no equilibrium condition can be attained and studied, the changes being transient in character and ending with the complete destruction of cementite.

Experimental

The raw material was a white cast iron of the following composition:

Carbon 2.30 per cent, Silicon 1.20 per cent

This material was used in an earlier investigation of graphitizing conditions.[4]

The A_{gr} line of this material is accurately known from that investigation. Its A_{cm} line may be approximated by considering it a straight line joining the pearlite point for the given silicon content as determined by Hayes and Wakefield[5] and the lower end of the eutectic line as determined by Gontermann.[6]

These methods are necessary for it is not possible to work as did Bates and Lawson, with two alloys differing only in carbon content. It cannot be postulated that under the present conditions not corresponding to any equilibria, two solutions in different alloys would be of the same composition. Nor can we proceed without making some assumption as to the density of the carbide. As a first approximation the value 7.5, an even figure near the value for Fe_3C, was chosen. There is here a certain possibility of error for which a partial correction may be made as described later.

The procedure consisted of heating specimens at various temperatures for a time sufficient to cause a fair degree of graphitization and quenching. The graphite was then determined gravimetrically and the density by the Archimedean principle. The volume percentage of the carbide phase was determined planimetrically by the intercept method. Evidently the data permit the calculation of the carbon content of the carbide phase assuming the solid solution to be either austenite or boydenite. The observational data and calculated results may be tabulated as follows:

[4]H. A. Schwartz, Payne, Gorton and Austin, "Conditions of Stable Equilibrium in Iron-Carbon Alloys," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 69, p. 791.

[5]Anson Hayes and H. U. Wakefield, "The Carbon Content of Pearlite in Iron-Carbon Alloys Containing One Per Cent Silicon," Transactions, American Society for Steel Treating, Vol. 10, 1926, p. 214.

[6]W. Gontermann, "Iron-Silicon-Carbon Alloys," *Journal*, Iron and Steel Institute, Vol. 83, No. 1, p. 421.

Table I

Temp. Deg. Cent.	Total Carbon	Graphite	Vol. of Carbide	Density	Carbon Concentration Austenite	Carbon Concentration Boydenite	Per Cent Carbon in Carbide if sol. is Austenite	Per Cent Carbon in Carbide if sol. is Boydenite
As cast	2.30	nil	26.0	7.714	0.62	....	7.27	....
740	2.30	0.05	16.7	7.702	0.62	....	10.7	....
780	2.30	0.48	15.0	7.639	0.72	0.56	8.21	9.13
824	2.30	0.15	17.5	7.656	0.85	0.66	8.44	9.35
858	2.30	0.06	20.2	7.668	0.94	0.76	7.52	8.25
880	2.30	0.23	16.2	7.659	1.00	0.82	7.76	8.71
894	2.30	0.05	20.1	7.665	1.04	0.88	7.19	7.85
938	2.30	0.10	15.2	7.660	1.16	1.04	8.15	8.83
976	2.30	0.16	16.1	7.667	1.26	1.17	6.86	7.34
1024	2.30	0.55	11.9	7.587	1.40	1.38	4.44	4.59
1075	2.30	0.71	8.8	7.592	1.54*	1.62*	2.24	1.41

*The carbon content of boydenite is almost certainly lower than that of austenite. The discrepancy is probably due to an inaccuracy in our assumptions as to the carbon content of silico austenite.

A constancy at high values of carbon concentration in the carbide up to about 900 degrees Cent. (1650 degrees Fahr.) is observable followed by a great decrease in carbon concentration with rising temperature.

It was thought that perhaps the high carbon carbide phase was decomposed analytically, graphite being obtained which did not originally exist as such. The volume per cent of graphite in one sample was checked by outlining the carbon spots in a photomicrograph and weighing the paper. A volume percentage about twice that corresponding to the analytical determination was obtained, perhaps due to opening out during polishing of the voids formed by carbon. This, though not good agreement, at least disposes of the possibility of some graphite originating by chemical attack.

The original hard iron and specimens quenched from 888 degrees Cent. (1630 degrees Fahr.) and 1050 degrees Cent. (1920 degrees Fahr.) were examined by the usual X-ray diffraction methods using the standard General Electric apparatus; the planar spacings being obtained by the reflection of the X-ray beam from the surface of a piece of each specimen are shown in Table II.

Discussion of Data

The following results were obtained from the reflection photographs:

(1) The alpha iron lines in the patterns of the specimens which had been quenched after treatment at 888 and 1050 degrees Cent.

Table II

Interplanar Spacings of a Sample of White Iron. Armco Iron Standard. Exposed 48 Hours

Spacings	Intensities	Remarks
2.36	Weak	
2.30	Very weak	
2.251	Weak	Probably Alpha Iron Kβ
2.20	Weak	
2.07	Weak	
2.05	Weak	
2.015	Very strong	Alpha Iron
1.96	Weak	
1.86	Weak	
1.844	Weak	
1.779	Weak	
1.755	Weak	
1.677	Weak	
1.63	Very weak	
1.60	Very weak	Probably Alpha Iron Kβ
1.58	Very weak	
1.504	Weak	
1.427	Medium	Alpha Iron
1.324	Weak	
1.31	Very weak	
1.253	Very weak	Questionable
1.215	Weak	
1.184	Very weak	
1.168	Strong	Alpha Iron
1.126	Weak	

Interplanar Spacings of White Iron, Quenched from 888 Degrees Cent. Armco Iron Standard. Exposed 48 Hours

3.94	Very weak	Questionable
3.52	Very weak	Questionable
3.32	Very weak	Questionable
2.82	Very weak	Questionable
2.71	Very weak	Questionable
2.60	Very weak	Questionable
2.52	Very weak	Questionable
2.42	Very weak	Questionable
2.37	Medium	
2.245	Weak	Checked line, possible Alpha Iron Kα
2.20	Medium	
2.09	Weak	Questionable
2.065	Very strong	Austenite
2.015	Very strong	Alpha Iron
1.953	Medium	
1.851	Medium	
1.795	Medium	Austenite
1.756	Very weak	Questionable
1.579	Weak	
1.63	Very weak	
1.579	Medium	
1.539	Very weak	
1.50	Weak	
1.423	Weak medium	Alpha Iron
1.316	Weak	
1.27	Weak medium	Austenite
1.22	Weak	
1.189	Very weak	Questionable
1.17	Medium	Alpha Iron
1.152	Weak	
1.125	Weak	
1.104	Weak	
1.085	Weak	Austenite

Table II (concluded)

Interplanar Spacings of White Iron, Quenched from 1050 Degrees Cent. Armco Iron Standard. Exposed 48 Hours

Spacings	Intensities	Remarks
2.61	Very weak	Questionable
2.51	Very weak	
2.37	Weak	
2.25	Very weak	Questionable, possible Alpha Iron Kβ
2.14	Very weak	Questionable, possible Alpha Iron Kβ
2.08	Very strong	Austenite
2.048	Medium	Questionable, checked line
2.020	Strong	Alpha Iron
1.965	Very weak	
1.854	Very weak	Austenite
1.809	Medium	
1.759	Very weak	
1.721	Very weak	
1.689	Very weak	
1.638	Very weak	
1.58	Very weak	
1.507	Very weak	
1.43	Weak	Broad line; Alpha Iron
1.329	Weak	
1.28	Medium	Austenite
1.217	Weak	
1.170	Medium	Alpha Iron
1.13	Very weak	
1.112	Very weak	
1.092	Medium	Austenite
1.048	Weak	Austenite
1.012	Weak	Alpha Iron
0.907	Weak	Alpha Iron

(1630 and 1920 degrees Fahr.) were wide and blurred due to distortion produced by quenching or possibly a very fine grain size. The ferrite lines in the unquenched iron were sharp and well defined.

(2) The sample quenched from 1050 degrees Cent. (1920 degrees Fahr.) contained considerably more gamma iron solution than the specimen quenched from 888 degrees Cent. (1630 degrees Fahr.). The gamma iron reflections in the film of the sample quenched from 1050 degrees Cent. (1920 degrees Fahr.) registered a decided expansion of the face-centered cubic lattice, Einar Ohman,[7] suggesting the interstitial introduction of solute carbon atoms.

(3) The sample quenched from 888 degrees Cent. (1630 degrees Fahr.) contained appreciably more cementite than the cast iron quenched from 1050 degrees Cent. (1920 degrees Fahr.). The cementite reflections in the pattern of the specimen quenched from 888 degrees Cent. (1630 degrees Fahr.) possibly indicated a slight contraction[8] of the cementite lattice as determined from the pattern

[7]Einar Ohman, "X-Ray Investigations on the Crystal Structure of Hardened Steel," *Journal*, Iron and Steel Institute, Vol. 123, 1931, No. 1, p. 445.

[8]The fact of such contraction has been more definitely observed by one of the authors in another connection. "Notes on Metastable Equilibrium in Hypereutectoid Iron-Carbon Alloys," Dolch and Ivanso, 1931, unpublished thesis, Department of Metallurgy, Case School of Applied Science, Cleveland.

of white cast iron. A lattice contraction would perhaps signify a simple substitutional introduction of carbon atoms. The parameter measurements of the cementite present in the specimen quenched at 1050 degrees Cent. (1920 degrees Fahr.) could not be accurately ascertained because of the very weak reflection due to the presence of the small quantity of the phase.

It has been suggested elsewhere[9] that boydenite may be a substitutional solid solution and austenite additive (i.e. interstitial). The observed expansion of the solid solution lattice suggests that it is austenite and creates a presumption in favor of the data calculated on that supposition. This presumption does not, however, amount to positive proof, and certain experiments were performed in order to determine whether the expansion could be otherwise accounted for.

A specimen of the same metal was quenched from stable equilibrium at 1000 degrees Cent. (1830 degrees Fahr.), that is after the cementite had completely disappeared. The interplanar spacings were then measured under the same conditions as before. For comparison the interplanar spacings of Armco iron both quenched and

Table III

Interplanar Spacings of Hard Iron, held to Equilibrium at 1000°C, then Water Quenched.

Spacings		Intensities	Remarks
2.08	A°	Strong	Austenite
2.024		Very strong	Alpha Iron
1.81		Medium	Austenite
1.433		Medium	Alpha Iron broad line
1.279		Medium	Austenite
1.173		Medium	Alpha Iron
1.092		Weak	Austenite
1.046		Weak	Austenite
1.017		Very weak	Alpha Iron
Interplanar Spacings of Armco Iron, Quenched from 1050 Degrees Cent. (1920 Degrees Fahr.)			
2.27	A°	Very weak	Kβ Alpha Iron
2.080		Very weak	Probably Austenite
2.026		Very strong	Alpha Iron
1.438		Strong	Alpha Iron
1.173		Strong	Alpha Iron
1.018		Medium	Alpha Iron
0.909		Medium	Alpha Iron
Interplanar Spacings of Armco Iron, Annealed from 1050 Degrees Cent. (1920 Degrees Fahr.)			
2.025	A°	Very strong	Alpha Iron
1.431		Medium	Alpha Iron
1.173		Strong	Alpha Iron
1.018		Medium	Alpha Iron
0.909		Medium	Alpha Iron

[9]H. A. Schwartz, "Evidences Concerning the Location of the Carbon Atom in Boydenite," TRANSACTIONS, American Society for Steel Treating, Vol. 11, 1927, p. 277.

annealed from 1050 degrees Cent. (1920 degrees Fahr.) were recorded. The data are tabulated in Table III.

The X-ray pattern of the white iron held at equilibrium at 1000 degrees Cent. (1830 degrees Fahr.) showed gamma iron solution lines which revealed a lattice identical in dimensions with the cell in the white iron sample quenched from 1050 degrees Cent. (1920 degrees Fahr.). The lattice is considerably larger than that of the iron quenched from 888 degrees Cent. (1630 degrees Fahr.) or the gamma iron lattice of pure iron obtained by extrapolation (Ohman, loc. cit.).

No difference in the alpha iron lattice dimensions of the quenched and annealed Armco ingot iron samples could be detected. The alpha iron lattices were similar to the white iron held at equilibrium at 1000 degrees Cent. (1830 degrees Fahr.) and are slightly larger than the calculated alpha iron lattice (Westgren). The white iron, quenched from 1050 degrees Cent. (1920 degrees Fahr.), alpha iron lattice was about the same and the white iron, quenched from 888 degrees Cent. (1630 degrees Fahr.), had dimensions possibly slightly smaller than the calculated. All the alpha iron lattice dimension variations were very small, only slightly above the limits of accuracy of the method and not of the same order of magnitude as the observed gamma iron parameter variations.

A very weak, but definite line occurred at 2.08 Å on the pattern of the quenched Armco ingot iron sample. This position cor-

Table IV
Interplanar Spacings in Angstrom Units

Austenite Reflections				
White Iron				
888°C (1630°F)	1050°C (1920°F)	1000°C (1830°F) Equilibrium	Calculated from Ohman's value 3.562 Å	Calculated from Jeffries' and Archer's value 3.60 Å
2.065*	2.08	2.08	2.057	2.078
1.795	1.809	1.81	1.781	1.800
1.27	1.28	1.279	1.260	1.273
1.085	1.092	1.092	1.074	1.084
1.040	1.048	1.046	1.028	1.038

Alpha Iron Reflections					
	White Iron				
Calculated from Westgren's value 2.8607 Å	888°C (1630°F)	1050°C (1920°F)	1000°C (1830°F) Equilibrium	Armco Ingot Iron Annealed	Armco Ingot Iron Quenched
2.023	2.015*	2.020	2.024	2.025	2.026
1.43	1.423*	1.430	1.433	1.431	1.438*
1.169	1.169*	1.170	1.173	1.173	1.173
1.012	1.012*	1.012	1.017	1.018	1.018
.906	.904*	.907	.909	.909	.909

*Wide Lines.

responds to the most intense austenite reflection. No other austenite lines could be detected. It is probable that this line is a gamma iron reflection and if so, the lattice would have about the same dimensions as the austenite cell of the white iron (1050 degrees Cent.) sample. The comparison is summarized in Table IV.

The data of Table IV, especially a comparison of the second and third columns, certainly do not permit of any conclusion as to whether the carbon concentration of austenite or boydenite should be used in computing the carbon content of cementite.

The data of Table II correspond to an average expansion of interplanar spacings of 0.76 per cent as between material quenched at 888 and 1050 degrees Cent. (1630 and 1920 degrees Fahr.). Depending on whether one takes the data for austenite or boydenite this amounts to an increase of carbon solubility of 1.3 or 1.9 atom per cents. According to the data of Wever[10] and assuming that in either case the solution is additive or interstitial, a lattice expansion of 0.36 per cent or 0.53 per cent is indicated. The observed expansion is one and one-half or two times the expected. We have calculated the expansion in this manner, hoping to exclude from the comparison any elastic expansion retained by rapid supercooling.

Ohman's data (Fig. 2 loc. cit.) show an expected expansion, between the specimens quenched from 888 and 1050 degrees Cent. (1630 and 1920 degrees Fahr.), of about 0.8 per cent as against the observed 0.76 per cent but require an expansion of 1.6 per cent in the gamma iron lattice due to its conversion into saturated austenite at 1050 degrees Cent. (1920 degrees Fahr.). The observed expansion is only 1.1 per cent.

The fact that in nearly pure iron the gamma iron lattice was apparently expanded as much (1.1 per cent) as in the presence of nearly 1.5 per cent combined carbon seems to cast further doubt on any correlation between carbon content and lattice dimension in such drastically quenched material. The observed expansion, 1.1 per cent, comparing the planar spacings of the specimen quenched from 1050 degrees Cent. (1920 degrees Fahr.) with the normal spacings is, nevertheless, identical with the value which would be predicted from Wever's Fig. 3.

It is not to be rashly concluded that the existence of an additive solution after drastic supercooling is evidence of its existence at the

[10]Wever, "Zur Kenntnis des Mischkristalles-Eisen-Kohlenstoff," Mitteilungen aus dem Institut für Eisenforschung, Vol VI, Part 1, 1925.

quenching temperature. This atomic arrangement characterizes the metastable solution and even if the stable solution be substitutional, it would be prone to pass over into the metastable as it becomes supersaturated during a rapid temperature decrease.

The diffraction data are not to be misinterpreted as a dissertation on the space lattice of boydenite. Contractions of lattice such as observed in cementite are believed to be fairly definite proof of changes of arrangement, as the sources of confusion all seem to result in abnormal expansions.

Consulting Table I we find by interpolation that if austenite be the solid solution at 888 degrees Cent. (1630 degrees Fahr.), cementite contains about 7.43 per cent carbon and the diffraction data show a decrease in lattice parameter of the order of magnitude of 2 in 1000, that is, a decrease in volume of about 0.6 per cent.

Consider now the effect on density of substituting carbon atoms for iron atoms and vice versa in the cementite lattice. Let there be "n" atomic per cent of carbon.

$$\text{Wt. per cent of carbon} = C = \frac{12\,n}{12\,n + 56(100 - n)} \times 100$$

$$= \frac{1200\,n}{5600 - 44\,n} \qquad (1)$$

$$\text{Mass per unit cell} = \frac{12\,n + 56(100 - n)}{100} \frac{16}{N} \qquad (2)$$

where N is Avogadro's number and 16 is the number of atoms in a lattice cell

$$= \frac{300 + 5600 - 1400}{100} \frac{16}{N}$$

$$= \frac{4500}{100} \frac{16}{N} \qquad (3)$$

for Fe_3C when n = 25.

$$\text{Sp. Gr. } (Fe_3C = 1) = \frac{12\,n + 5600 - 56\,n}{4500}$$

$$= \frac{5600 - 44\,n}{4500} \qquad (4)$$

Solve (1) for n in terms of C and substitute in (4)

$$n = \frac{5600\,C}{1200 + 44\,C}$$

$$\text{Sp. Gr. } (Fe_3C = 1) = \frac{56}{45}\,\frac{1200}{1200 + 44\ C} \qquad (5)$$

Since the accepted density of Fe_3C is near 7.66 and quenched from 888 degrees Cent. (1630 degrees Fahr.) the lattice cell is diminished in volume by about 0.6 per cent the density of any substitutional solution quenched from 888 degrees Cent. (1630 degrees Fahr.) will be

$$= 1.006 \times 7.66\ \frac{56}{45}\,\frac{1200}{1200 + 44\ C}$$

$$\rho = 9.586\ \frac{1200}{1200 + 44\ C} \qquad (6)$$

substituting for C the first approximation of its value 7.43, and

$$\rho = 7.536$$

which is believed as good a verification of the first approximation, 7.5, as the data justify, especially considering the fact that the silicon content has not been considered.

Reasons will be cited later for considering the cementite quenched from 1050 degrees Cent. (1920 degrees Fahr.) as Fe_3C from which some carbon atoms have been removed.

Assuming the lattice parameter to be identical with that of the material quenched from 888 degrees Cent. (1630 degrees Fahr.), which can hardly be more than a few per cent in error, the following calculation can be made. Call L the loss in per cent of the original weight of Fe_3C, of carbon from the original cementite; then if C be the per cent carbon in the final product,

$$C = \frac{100(6.67 - L)}{100 - L} \qquad (7)$$

and the density will be

$$\rho = 1.006 \times 7.66 \times \frac{100 - L}{100} \qquad (8)$$

combining (7) and (8)

$$\rho = 7.706\ \left(1 - \frac{6.67 - C}{100 - C}\right) \qquad (9)$$

Applying this equation to the data for 1024 degrees Cent. in Table I

$$\rho = 7.523$$

which is again sufficiently close to the assumed 7.5 to require no further correction.

Interpretation of Results

Hendricks[11] considers that the cementite lattice consists of a orthorhombic cell, carbon atoms being located at each corner, at the middle of each long edge, at the centers of the smallest faces and at the center of gravity of the cell. Each carbon atom is surrounded by six iron atoms arranged at the points of an octahedron whose center of gravity is the carbon atom. Adjacent octahedra share an iron atom. Iron and carbon atoms have radii closely identical with those they have in austenite. It is our understanding that Westgren (personal conversation) regards these conclusions as generally justified by the data.

We have shown that when white iron is heated sufficiently to produce notable amounts of graphite the remaining cementite is identical in crystallographic type with Fe_3C but the unit cell has become slightly smaller. The substance has decreased in density and increased in carbon content. The facts are in accord with the view that "cementite" in partially graphitized iron at 888 degrees Cent. (1630 degrees Fahr.) is a solution of carbon in Fe_3C in which carbon atoms are substituted for iron atoms. At higher temperatures the carbon content decreases to far below that of Fe_3C, the lattice type is still that of Fe_3C but its dimensions cannot be accurately determined. They certainly have not changed *very* greatly.

Substitution of iron for carbon atoms could not occur, on account of their great difference in size, without marked changes of parameter. Additive or interstitial iron atoms are still less possible with an unchanged lattice. The only possible solution occurring to us is that the "cementite" arrangement may possess some degree of stability even without the carbon atoms at the centers of the octahedra.

This explanation involves the anomaly that first carbon atoms crowd into the lattice structure and then leave it. Any alternative hypothesis would be open to the same objection since the observed facts are first an increase and then a decrease in carbon content.

The silicon content can at most be a contributing factor for

[11] Hendricks, "The Crystal Structure of Cementite," *Zeitschrift für Kristallographie*, Vol. 74, Part 5/6.

Bates and Lawson observed high carbon cementite in graphitizable alloys very low in that element. That they did not observe it at lower temperatures is perhaps due to the trivial amount of graphitization occurring there.

The data shown graphically in Fig. 1 as to the general form of the curve correlating carbon concentration of cementite with temperature would not be altered by any plausible changes in the assump-

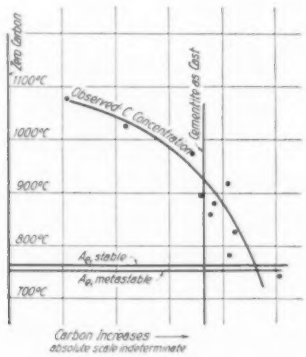


Fig. 1

tions as to the carbon content of the solid solution. The absolute values of the cementite carbon concentration depend, however, entirely upon the concentrations adopted for the solid solution.

The A_{gr} line underlying our work is capable of accurate chemical determination. This is not equally true of the A_{cm} line. We have based our conclusions upon what we regarded as the best established published information without assuming responsibility for the accuracy of such data.

If one assumes that cementite below A_1 even in the presence of silicon should contain $6\frac{2}{3}$ per cent carbon, then the eutectoid carbon concentration works out as 0.82 per cent carbon. Values comparable with those of the binary system are thus obtained. Substituting this value for that of Hayes and Wakefield, the carbon concentration of cementite at 740 degrees Cent. (1365 degrees Fahr.) becomes 9.63 per cent instead of 10.7 per cent and at higher temperatures the correction becomes less. Between 850 and 950 degrees Cent. (1560 and 1740 degrees Fahr.) carbon concentrations in the cementite would be obtained of the general order of magnitude of that corresponding to Fe_3C.

Since a priori there is no basis for the assumption that the presence of 1.2 per cent silicon does not alter the equilibria in the iron-carbon system these considerations need not be regarded as a

criticism of the Hayes-Wakefield data. They are merely referred to in elucidation of the relation between the carbon concentrations of cementite and solid solution.

Other grounds exist for not unreservedly adopting the Hayes-Wakefield figure and assigning absolute values to the carbon content of cementite at various temperatures, even assuming that the limit of solubility of carbon in Fe_3C has been obtained.

(1) Some years ago M. M. Austin, under the senior author's direction, observed that in the presence of about 1.2 per cent silicon, steel near 0.92 per cent carbon was nearly of eutectoid structure.

(2) Reed[12] was unable to secure satisfactory data in the Fe-C-Si system.

(3) Söhnchen and Piwowarsky,[13] in an investigation of the effect of silicon on the composition of the stable iron-carbon eutectoid expressly point to the fact that their data check those of Hayes and Wakefield. The German workers ignore the fact that the latter's intention was to determine the metastable eutectoid point and that such an agreement would not be expected since the stable eutectoid should lie to the left of the metastable. It may, of course, be that Hayes and Wakefield unexpectedly realized the stable system. If this be so, their data do not conform to our desire to use the carbon concentration of the metastable system. Alternatively, the Germans may have unknowingly passed into the metastable system and confirmed the American data. We are unable to decide this question satisfactorily from the data available.

(4) In attempts in connection with the present paper to redetermine the eutectoid concentration in 1.2 per cent silicon steel by Hayes' method except that the specimens were also examined after annealing, very erratic results could be obtained. A steel containing 0.65 per cent carbon might freeze slowly and appear nearly eutectoid but after annealing planimetric measurements evaluated in the manner of Hayes and Wakefield gave values somewhat above 0.90 per cent carbon. Specimens of ordinary fairly low silicon rolled steels could not be made to yield concordant results. A 0.23 per cent carbon steel gave 1.18 per cent carbon in the eutectoid. A 0.49 per cent carbon

[12]E. L. Reed, "Influence of Special Elements on the Carbon Content of the Iron-Carbon Eutectoid," TRANSACTIONS, American Society for Steel Treating, Vol. 20, No. 2, 1932, p. 115.

[13]Söhnchen and Piwowarsky, "Ueber den Einfluss der Legierungselemente Nickel, Silizium, Aluminium und Phosphor auf die Löslichkeit des Kohlenstoffs im flüssigen und festen Eisen," *Archiv für das Eisenhüttenwesen*, Vol. 5, 111, 1931-32.

gave 0.68 per cent. A vacuum-melted cast and annealed steel containing 0.67 per cent carbon, 0.10 per cent silicon gave 1.12 per cent carbon in the eutectoid. Lacking knowledge of whether the austenite or boydenite equilibrium is involved and being unable to confirm accepted data as to the eutectoid point, it appears safest not to attempt the assigning of absolute carbon values for the two phases involved.

Mechanism of Incipient Graphitization

It seems proven that when a graphitizable mixture of iron carbide and alpha iron is heated above A_1 after a sufficient lapse of time the following changes have occurred.

1. Alpha iron has changed to gamma iron.

2. Some carbon or cementite has gone into solution in gamma iron to form a solid solution. Whether in austenite the carbon atom plus the six iron atoms located at the center of the enclosing cubic cell represent one of the original octahedra of the cementite is an interesting speculation.

3. Some cementite has been decomposed into carbon and gamma iron and the carbon atoms have displaced iron atoms, iron atoms resulting from both reactions becoming the solvent for forming more solid solution, still further reducing the amount of cementite. This mechanism is perhaps responsible for the observations of Schüz and Stotz. Possibly there is a limiting carbon concentration in cementite, which may or may not be reached before all the carbon finally crystallizes out as graphite. If the Hayes-Wakefield data for the eutectoid composition are reliable, such a concentration is in excess of 8 per cent just above A_1 and may be much in excess. The compound Fe_2C often referred to may represent merely the resulting maximum solubility corresponding to the substitution of one carbon for one iron in every unit cell.

4. With increasing temperature (and time?) carbon atoms leave the cementite cell to crystallize out in the free state. This depletion may go even to the point of removing some of the atoms originally required in the Fe_3C arrangement before the structure changes to gamma iron throughout.

5. The crystallization of free carbon with liberation of gamma iron, of course, occurs parallel with all these reactions.

Conclusions

It is believed to be shown that temperatures near but not neces-

sarily above A_1 "cementite," at least in graphitizable alloys, is not a definite chemical compound but varies in carbon content with the temperature. A sudden increase in carbon followed by a continuous decrease of carbon with temperature is noted. The rate of decrease increases greatly with temperature above about 950 degrees Cent. (1740 degrees Fahr.). This may be visualized as a solution of gamma iron in a solution of carbon in cementite although this concept is intended only as a picture and is not for rigid acceptance.

All cementites, including Fe_3C, have similar space lattices but not identical parameters. At least in the lower ranges above A_1 the parameter is decreased by the additional carbon content. A mechanism for the conversion of Fe_3C into other products of graphitization is outlined.

It is suggested that cementite and iron carbide are not synonymous, the former being of indefinite composition characterized by a given lattice type, the latter a special case having the composition Fe_3C.

DISCUSSION

Written Discussion: By R. H. Harrington, research metallurgist, General Electric Co., Schenectady, N. Y.

Many investigators have struggled, in private and in publication, with the behavior of iron-carbon alloys during graphitization. The conclusions have been rather varied and considerable mystery yet remains. Any attempt to analyze these reactions is deserving of commendation.

X-ray technologists are generally in agreement that X-ray work of the type undertaken by the authors is usually of concise value only when corroboration is possible by some other means.

The use of the planimeter to determine volume percentages of phases in equilibrium structures is not open to much question. Certainly great care must be exercised in obtaining consistent and accurate data concerning non-equilibrium structures by such a method.

It is interesting to note that the authors have found the carbon content of the carbide phase to first increase and then to decrease. It seems that this might indicate the resultant action of two different reactions, one being negligible at the lower temperatures and predominant at the higher temperatures.

Erich Scheil[1] has recently shown that with graphitization there is a marked tendency for the silicon in solid solution bordering the graphite to be oxidized to silicic acid or to a silicate. This results in the possible addition of the elements silicon and oxygen to the carbide phase. This causes continued diffusion of silicon to the graphitizing carbide phase and is effective with relatively small silicon percentages. This reaction would be slower with smaller precentages

[1] "Untersuchungen "Über das Wachsen von Gusseisen," von Erich Scheil, *Archiv für das Eisenhüttenwesen*, August, 1932.

of silicon and faster at the higher temperatures. Perhaps this should not be overlooked as a contributing factor to the lower carbon content of the carbide phase as quenched from the higher temperatures. Photomicrographs of the alloys would be of great interest.

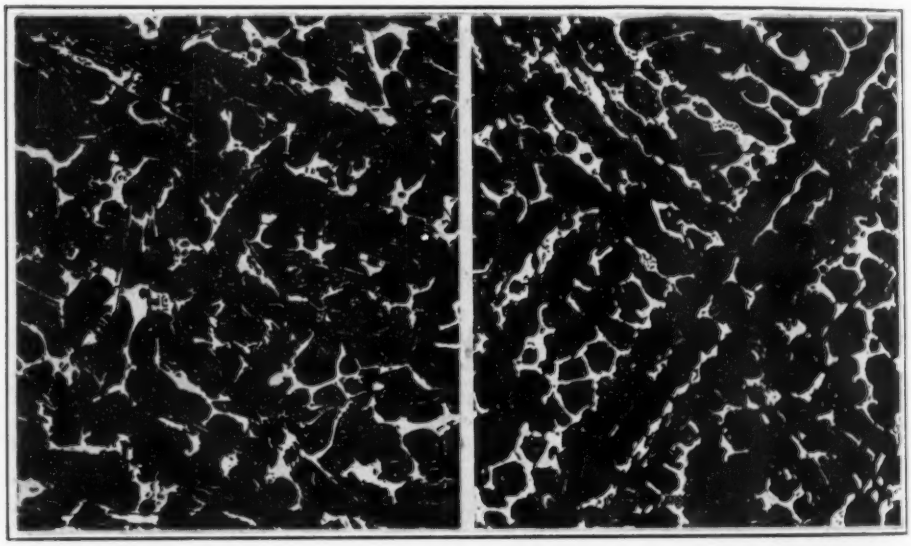
Might it not be possible to quench filings of the alloys (studied by the authors) from the different temperatures and to thus obtain by more drastic cooling quenched structures even more closely akin to those existing at the quenching temperatures? X-ray spectra of these filings might yield equally interesting data.

The authors are deserving of commendation for their attack on so elusive a problem and they should be encouraged to continue this type of work.

Authors' Closure

It is gratifying to note sufficient interest by another in our problem to bring out as many fruitful suggestions as are submitted by Dr. Harrington.

At his suggestion two photomicrographs are appended showing the metallographic characteristics of the metal when quenched from two ranges, one corresponding to abnormally high and another to abnormally low carbon contents.



Left—Quenched from 824 Degrees Cent.
Right—Quenched from 1024 Degrees Cent.

In order to obtain contrast in these negatives the specimens were drawn very briefly at low temperatures in order to start the conversion of martensite to troostite and produce a darker background upon etching.

It will be understood that the planimeter work on these specimens was done at magnifications three and one-half times greater than the 100 diameters at which the photographs were made.

The writer does not understand clearly in what respect planimetric observations should be different depending upon whether certain structures are equilibrium structures or nonequilibrium structures. It is, of course, clear that interpretation from the results of planimetric data involve assumptions as to

uniformity of composition and so on which may or may not be realized if the structures are not known to be in equilibrium. Since the actual obtaining of these areas is purely a problem of geometry it would seem to make no difference what the substances were whose areas were being measured.

It is, of course, obvious that the carbon contents assigned by us to the various cementites are in the last analysis average carbon contents and no demonstration has been attempted that any given cementite grain is homogeneous throughout.

It is not believed that any concept as to nonuniformity of composition would alter the main conclusions of the paper as to the successive changes of carbon concentration with rising temperature.

This laboratory has had some experience with three different planimetric methods; the polar planimeter, the intercept planimeter in a special form designed here, and for certain special purposes the weighing of the paper corresponding to the areas of the desired constituent in a print after these areas have been cut out from the rest of the sheet.

We have often been tempted to devise also a photometric method but have never done so.

The polar planimeter is excellent when the measured constituent is of fairly good size and at least approximately equiaxed. In cases of finer distribution and especially of thin structures appearing as needles in a picture, it is nearly useless because of the difficulty and labor involved in following exactly the outlines.

Among the essentials of planimetry is the study of a considerable area in a given specimen and any method which will encourage measurements on rather large areas is to be recommended.

The length of traverse of our planimeter is ten inches and we have generally run eight traverses for every photomicrograph at 350 diameters. Usually for a given specimen at least four photomicrographs have been made in different portions of the specimen. It can therefore be seen that the average figures given represent the study of a fair amount of material in each case. No such complete survey would be possible with any polar planimetric method.

It has been suggested in personal conversation with Dr. Maurice Becker that the change of composition may be associated with the Curie point. We have made no attempts to check this suggestion but have had the general opinion that the increased carbon at low temperature occurred as the initial stage of graphitization irrespective of any particular temperature.

Possibly one would wish to consider Dr. Harrington's suggestion of two reactions as representing the solubility of gamma iron and of carbon respectively in iron carbide.

We are slightly familiar with the work of Scheil referred to by Dr. Harrington, having had some occasion to experiment in similar fields. We greatly question whether any oxidation to silicic acid or silicates has occurred in our material. Mr. Scheil found this true principally where flaky graphite was present, whereas in our specimens the graphite is nodular and present in relatively minute amounts as may be seen from the compositions.

Furthermore, the heat treatments are of short duration and carried on at pressures of a few millimeters of mercury so that little air should be available

for oxidation. Having in mind that an ordinary malleable heat treatment may oxidize about a quarter of a per cent of silicon to SiO_2 in the outer layers of a white iron casting being annealed and that this oxidation is limited to a layer of a few hundredths of an inch thick, we scarcely anticipate any interference from this phenomenon.

It is understood from later conversation with Dr. Harrington that he attaches importance also to the possibility of silicon acting directly to alter the composition of phases which are or are trying to become an equilibrium system.

If it can be shown that the very low carbon cementites are only encountered in the presence of silicon an explanation might be sought along the lines of an assumed substitution of silicon for carbon atoms in cementites at high temperatures. During the time elapsing between the reading and printing of the paper there has been time to perform a few key experiments.

A white iron free from silicon but capable of graphitization was prepared by first melting wash metal with some 0.30 per cent manganese to combine with its sulphur and also to remove the grosser oxygen content. The alloy was remelted in a magnesia crucible in the Arsem furnace with enough ferrozirconium to furnish about 0.30 per cent zirconium. Such an alloy proved to be mottled and it was, therefore, remelted in air and poured on an iron plate to promote rapid freezing. Such an alloy can scarcely contain over 0.05 per cent silicon and is probably considerably lower in zirconium than the calculated amount.

During a few minutes at 1050 degrees Cent. it graphitizes measurably containing 0.11 graphite. The carbon content of its cementite was 5.84 by the usual method of evaluation. It must be noted, however, that the degree of graphitization is much less than in those alloys showing very low carbon cementite described.

A repetition of the experiment using a time at 1050 degrees Cent. during which 0.31 per cent graphite separates, i.e., about three times as much as before, gave a carbon content of cementite of 5.27. In the former case the per cent cementite by volume was 33.62, in the latter 33.40 and since in the former case the mass is 0.1 per cent by volume graphite and in the latter 0.9 per cent, the per cent cementite referred to the volume of metal (total graphite) is still more nearly like 33.73 as against 33.65. It thus appears that in these stages of graphitization the volume of cementite is not decreased as graphite separates.

A similar experiment conducted on a melt of wash metal and ferrosilicon containing 0.47 silicon and held at 1050 degrees Cent. to produce 0.03 per cent graphite gave a carbon content for cementite of 6.48 per cent; the solid solution in this as in the preceding case being assumed to contain 1.5 per cent carbon. The value is, perhaps, slightly high in the presence of silicon and hence the value 6.48 is, perhaps, a little low.

Since the atomic weight of zirconium is 7.6 times that of carbon, the total amount of zirconium added to the melt could not substitute, atom for atom, for 0.31 per cent carbon separating as graphite even if there were room for such substitution in the cementite lattice.

We are thus inclined to believe that the decrease in carbon content of cementite is an accompaniment of the graphitizing process not necessarily involving the introduction of stranger atoms into the cementite molecule. This is not to say that the process may not be facilitated by such substitution.

THE NATURE AND PREVENTION OF INTERGRANULAR CORROSION IN AUSTENITIC STAINLESS STEELS

By E. C. Bain, R. H. Aborn, and J. J. B. Rutherford

Abstract

This paper sets forth detailed observations on the development of the characteristic intergranular susceptibility to corrosive attack in austenitic stainless steel, with special attention to the time-temperature relations in the heating causing the deterioration. Susceptibility is quantitatively reported as measured by loss of electrical conductivity in a standard corrosive medium. The paper interprets these data as pointing to a definite explanation of the phenomenon in terms of local depletion of useful chromium attending chromium-rich carbide formation.

Methods for obviating this undesirable behavior of the alloy are discussed with sufficient data to explain the mechanism of the remedies. The prevention of serious chromium-rich carbide formation by means of ample provision for the fixing of carbon by other carbide-forming elements is set forth with special reference to the necessity for heating the alloy so as to insure selective carbide precipitation. Here again the necessity for the time-temperature concept or the rate-of-reaction viewpoint is set forth.

The failure of magnetic changes, in the general sense, to parallel the development of susceptibility to intergranular attack is discussed with the thought of caution against the general use of magnetic tests to detect intergranular susceptibility.

Introduction

ONE of the few shortcomings of the austenitic stainless steels of the 18-8 type, particularly in the product of early manufacture, has caused considerable anxiety. The metal, after exposure to moderately elevated temperature in the general vicinity of 1000 to 1500 degrees Fahr. (500 to 800 degrees Cent.), has frequently been found to be subject to a very characteristic form of intergranular corrosion, even in environments which ordinarily have no effect upon the normal alloy. Thus, metal near a weld sometimes

The authors, who are members of the society, are associated with the Research Laboratories of the U. S. Steel Corporation at Kearny, N. J., Manuscript received March 22, 1933.

literally disintegrated in use with solutions which did not attack the remainder of the article; or sheets of the alloy would suffer loss of strength during pickling after an improper heat treatment had been permitted. Whenever metal was found to exist in the condition "sensitive" to intergranular attack, it could be restored to the normal corrosion resisting state by heating to somewhat higher temperature, e.g., 1650 to 2000 degrees Fahr. (900 to 1100 degrees Cent.), followed by rapid cooling. Inquiry into the circumstances preceding disintegration invariably discloses the controlling factor to have been a heating in the damaging range of temperature. Investigations here and abroad resulted in ascribing this unfortunate behavior to the reactions involved in carbide precipitation and solution and a comparatively simple, effective remedy has been developed.

The hypothesis which appears to explain both the symptoms and the remedy, postulates that the carbon largely dissolved at high temperature and permanently retained in supersaturated solution at ordinary temperatures is rejected in the form of a chromium-rich carbide in the grain boundaries at intermediate temperature. The formation of such a carbide draws heavily upon the chromium content of metal adjacent to a carbide particle, thereby impoverishing it in chromium below the concentration required for normal corrosion resistance. Accordingly, a vulnerable pathway through the metal is opened up along the grain boundaries wherever fine carbide precipitation occurs. Clearly, the separation of only chromium-rich carbide can cause this state of affairs, and if the carbon could be induced to withdraw from solid solution without its quota of chromium, then the alloy would not deteriorate. This can be accomplished by the presence, in sufficient proportion, of an element capable of forming its own carbide to the substantial exclusion of chromium carbide. The elements, titanium, columbium,[1] and probably tantalum, in adequate concentration, combine with most of the carbon, greatly reducing the carbon solubility; an entirely negligible chromium depletion then occurs; and this alloy is not subject to intergranular corrosion. The nature of the phenomenon of carbide

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[1]Dr. E. Houdremont in conversations in 1931 informed us of Krupp's experience up to that time as to the general effectiveness of titanium addition in lessening susceptibility to intergranular corrosion.

The writers are informed through communications from the Union Carbide and Carbon Research Laboratories that columbium additions completely eliminate intergranular corrosion with no significant impairment of physical properties and that the addition of columbium by ferrocolumbium is easy and efficient. Tests by the authors show that, in the samples of columbium-bearing material received from the Union Carbide and Carbon Research Laboratories, no sensitization was developed after heating for 1000 hours at temperatures within the range 400 to 1500 degrees Fahr. (200 to 815 degrees Cent.).

precipitation is set forth in the succeeding paragraphs in some detail, as a basis for explaining the action of titanium[2] addition as a remedial agent.

Characteristics of Sensitive Metal

Intergranular corrosion is not restricted to austenitic stainless steel, but may be discerned likewise in aluminum and copper alloys, and even in low carbon iron, after immersion in solutions which, for any reason, etch away the grain boundary material much more rapidly than the metal of the grains themselves. It is by no means surprising that corrosion should proceed in this manner, since the grain boundary is the initial location of many reactions which tend to alter the local composition or constitution of the alloy and thereby induce local difference in solution pressure. Metal which has suffered corrosive attack at the grain boundaries may appear essentially undisturbed, yet it will be found to possess reduced strength, and, if the attack is severe, to have lost its characteristic metallic "ring"; bending or twisting causes innumerable cracks which can be identified as intergranular, or whole grains may fall away from the specimen. Fig. 1 shows a photomicrograph of disintegrated metal. If the attack has penetrated through and through, the metal may even crumble to powder, the particles of which are the crystal grains of the metal. The electrical resistance of metal from which even the thinnest imaginable films of grain boundary material have been dissolved is tremendously increased, and a resistance determination proves to be an accurate measure of the depth of penetration of the intergranular attack. Figures for depth of penetration used in this discussion were obtained in this manner.

The various factors having to do with susceptibility to intergranular attack are discussed under the various headings below and constitute what might be termed "the data of intergranular corrosion." It may be advisable to state explicitly that at no point in this discussion is any reference made to the normal or general corrosion resistance of stainless steel. The data refer exclusively to a purely intergranular corrosion in a medium—copper sulphate-sulphuric acid solution—which causes no loss in weight on normal (unsensitized) metal, but which is adjusted in concentration to produce the severest possible intergranular attack upon sensitive mate-

[2]Most of the experience of the writers has had to do with titanium-bearing metal and the titanium behavior is therefore described. It is not believed that the reactions with other strongly carbide-forming elements such as columbium, or even uranium, would differ greatly except perhaps with respect to the actual concentrations involved.

rial.[3] The susceptibility of the intergranular metal, with respect to its failure to equal in resistance the normal grains themselves, is the only factor tested, and this is, in all cases, evaluated by the change

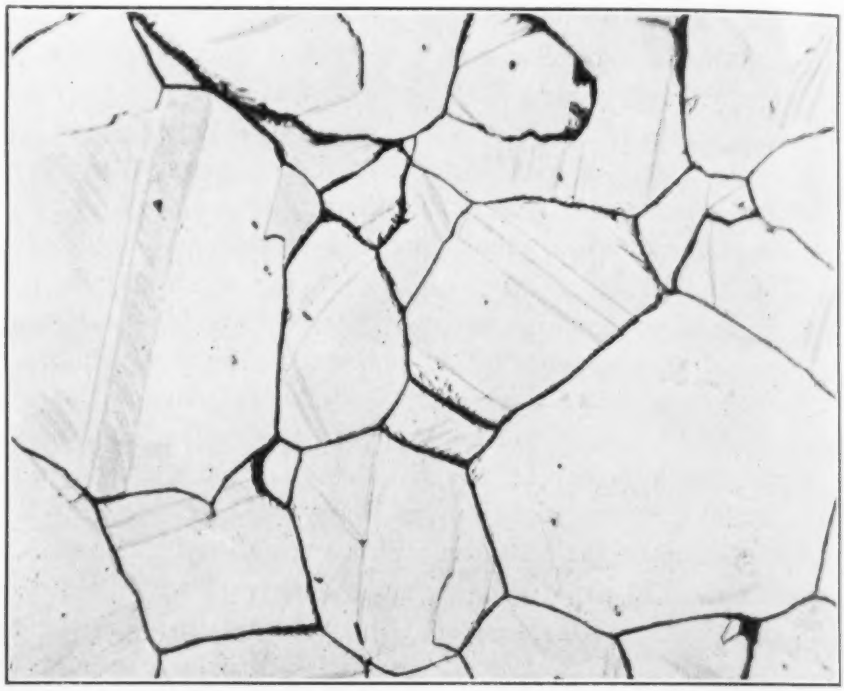


Fig. 1—Photomicrograph of Disintegrated Metal, After Sensitization and Corrosion. × 100.

in electrical resistance caused by the stated immersion in this particular corrosive medium.

Temperature and Time-interval Relations in Sensitization—The location of the familiar zones susceptible to intergranular attack on either side of a weld immediately suggests that an intermediate temperature is responsible for the loss of corrosion resistance. The

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[3]The change in electrical resistance of a specimen, as measured before and after immersion in a boiling solution of 47 c.c. Sp. Gr. 1.84 H_2SO_4, 13 gm. $CuSO_4.5H_2O$ per liter, supplies a measure of penetration. Correlation of results of many tests indicates that for specimens ⅛ inch in diameter, for example, the following relation between resistance increase and penetration holds.

$$\frac{\text{Res. (final)}}{\text{Res. (orig.)}} = \frac{.0491}{.0491 - 1.57p + 12.6p^2}$$

in which p = penetration (inch).

The usual time of immersion depends upon the degree of sensitization varying from 2 or 3 hours to several hundred hours. The penetration is computed to mils per 100 hours on the basis of a linear time relation, found to hold satisfactorily over the range of penetration employed. This test for susceptibility is certainly vastly more sensitive than is ordinarily required, and the lower range of figures is significant chiefly in developmental work or in applications of the alloy in contact with extremely corrosive environments. See Rutherford and Aborn, *Transactions*, A. I. M. E., Vol. 100, 1932, p. 293.

extent of this temperature range may be seen in Fig. 2, which shows the penetration in metal heated for 2 minutes, for 1 hour and for 1000 hours at a series of constant temperatures covering a wide range. The metal is rendered sensitive very slowly at such low temperatures as 1000 degrees Fahr. (540 degrees Cent.) and very rapidly at temperatures as high as 1400 degrees Fahr. (760 degrees

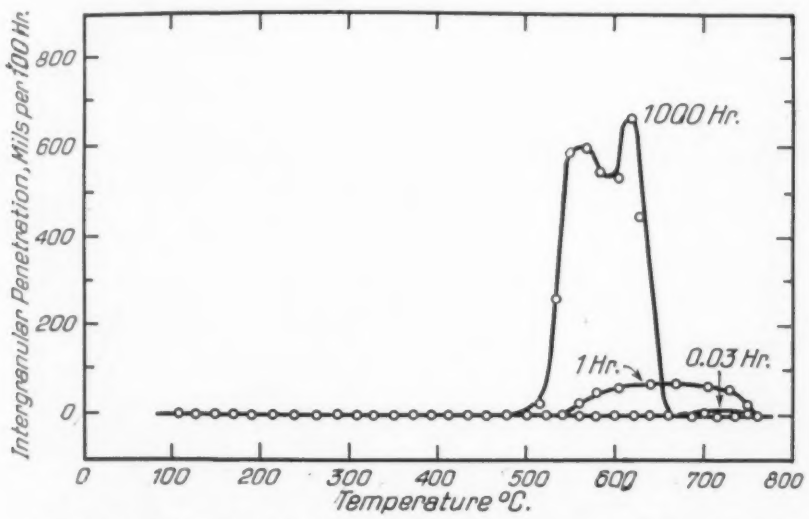


Fig. 2—Sensitivity Measured as Penetration in 100-hour Corrosive Attack, as Developed in 2 Minutes, 1 Hour, and 1000 Hours at a Series of Constant Temperatures. Alloy Composition, Chromium 18.1, Nickel 8.9, Carbon 0.08.

Cent.). The chart also shows that at temperatures above about 1180 degrees Fahr. (640 degrees Cent.) the metal, at first highly sensitized, is later gradually restored. This observation, further exemplified in Fig. 3, is significant in providing an important clue to the role of diffusion in this phenomenon, as later described. For each time interval of heating (at constant temperature) there is one particular temperature which induces the severest susceptibility. The time-temperature combination for maximum sensitivity is shown in Fig. 4, along with the degree of penetration resulting from this maximum.[4]

Carbon Content—That the development of a condition in the 18-8 alloy wherein corrosion proceeds rapidly along the grain boundaries is greatly influenced by the carbon content can be seen in Fig. 5. Heating for 1000 hours at the severest temperature pos-

[4]Tests carried to a 5200-hour heating interval confirm the trend indicated in the penetration curve of Fig. 4, that little if any increase in degree of sensitization occurs after a 1000-hour heating.

sible induces in the low carbon alloys only a fraction of the susceptibility found in the higher carbon alloys. That neither the chromium content within the range 15 to 19 per cent, nor nickel within the range 7.5 to 11 per cent, nor the sum of the two (100%—

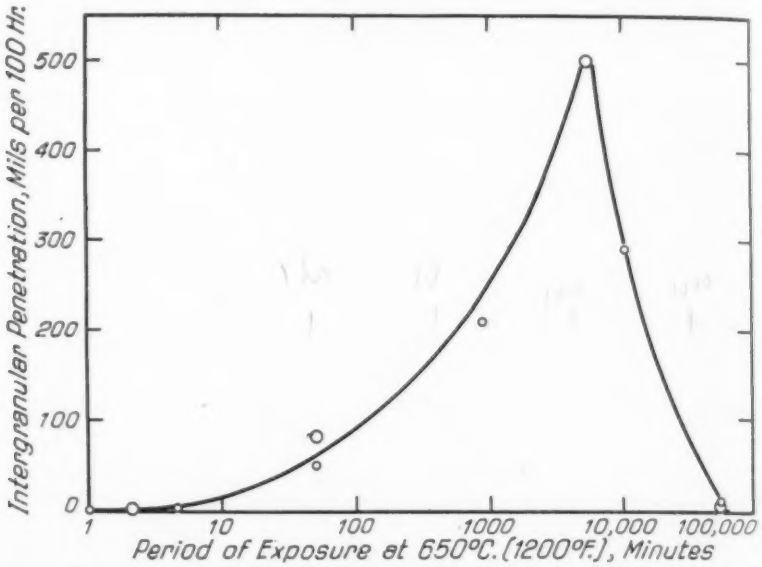


Fig. 3—Sensitization and Restoration at 1200 Degrees Fahr. (650 Degrees Cent.). Carbon Content 0.08 Per Cent.

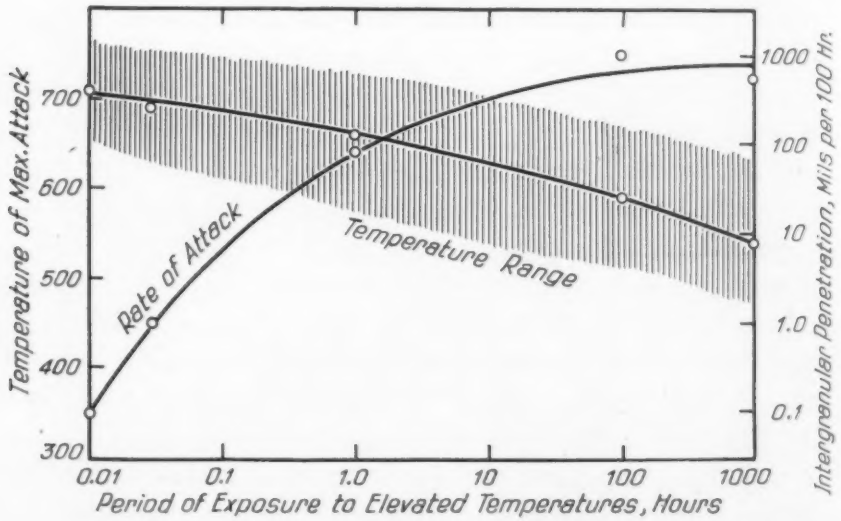


Fig. 4—Time-temperature Interval Relationship for Maximum Sensitization, and Degree of Maximum Sensitization thus Induced.

"residual iron") has any significant effect may be inferred likewise from an inspection of the figures of Table I, in which the attack parallels the carbon content, but shows no correlation with the nickel,

Table I

Analysis of Alloy				Maximum Intergranular Penetration Mils/100 hours (after 1000 hours heating)
C	Cr	Ni	Cr + Ni	
0.035	15.5	8.1	23.6	160
0.04	19.2	7.7	26.9	370
0.05	17.4	8.8	26.2	390
0.06	16.3	8.4	24.7	490
0.07	17.5	8.9	26.4	620
0.08	16.5	11.3	27.8	580
0.08	18.1	8.9	27.0	670
0.10	18.6	9.0	27.6	900
0.14	16.5	8.6	25.1	1450
0.20	17.5	8.6	26.1	1750

chromium, or iron content of the alloys. Experiment indicates that the alloys carrying less than about 0.02 per cent carbon are entirely free from intergranular attack.

Grain Size Influence—It has been observed[5] that a very fine grain in the austenitic steel predisposes the alloy to a retarded sensitization. The comparison curves of Fig. 6 illustrate this influence

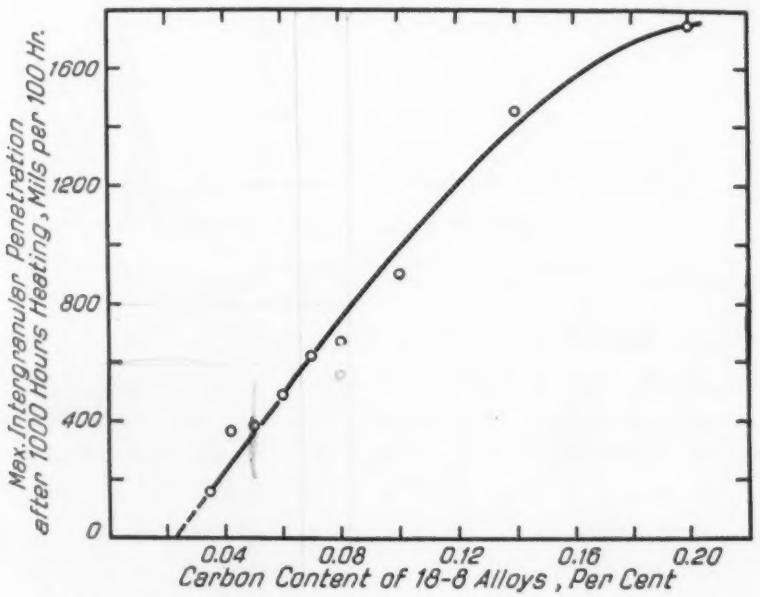


Fig. 5—The Dependence of Maximum Sensitivity Upon Carbon Content.

of grain size. This observation suggests that some influence upon the process of sensitization may be exerted by the relative proportion of normal crystalline material and grain boundary material. The grain size influence is most marked in the sensitization resulting

[5]Newell, H. D., TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 673.

from relatively short-time exposures to the damaging temperatures; whereas material heated for thousands of hours is severely affected without much regard to grain size.

Ferrite Formed During Sensitization—In many samples of the 18-8 alloy a definite response to a magnet is exhibited by metal in the sensitive state. In a few cases, as the metal becomes more and more susceptible to attack (either through maintenance at the damaging temperature for longer and longer intervals, or through heating for a constant time-interval at successively more injurious temperatures)

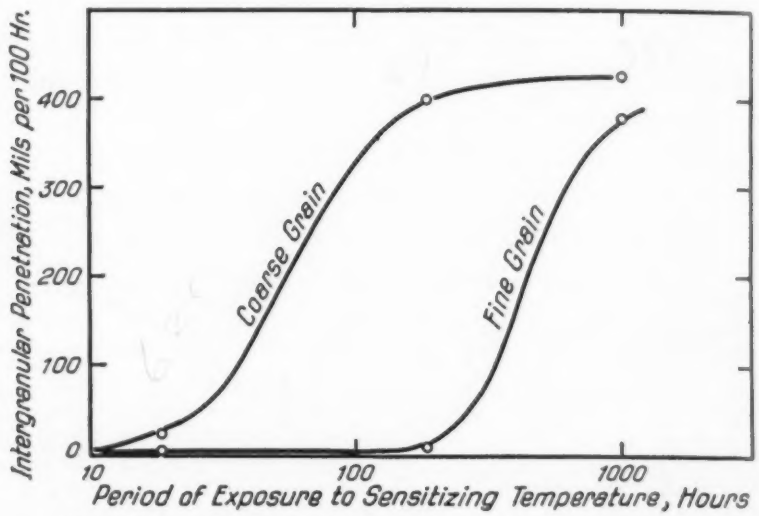


Fig. 6—Relative Development of Sensitivity in Coarse and Fine-grained Alloys. Chromium 17.6, Nickel 8.8, Carbon 0.05.

the magnetic induction similarly increases. In the higher nickel alloys, however, the sensitive condition is developed without the simultaneous production of magnetic material (ferrite), and a magnetic test is, therefore, no general criterion of sensitiveness in the alloy. The curve of Fig. 7 shows that considerable magnetic induction is developed in an 18-8 alloy during the period of sensitization, but no measurable induction is found in an 18-12 alloy of similar carbon content. It would scarcely be expected that susceptibility would be closely correlated with magnetic properties in a broad sense, although in individual cases it may appear to do so. Changes in alloy composition, particularly with respect to the relative amounts of chromium and nickel, exert a profound influence upon the production of the magnetic ferrite phase during sensitization, although the same changes of composition have very little effect upon the intergranular deterioration. In general, a higher

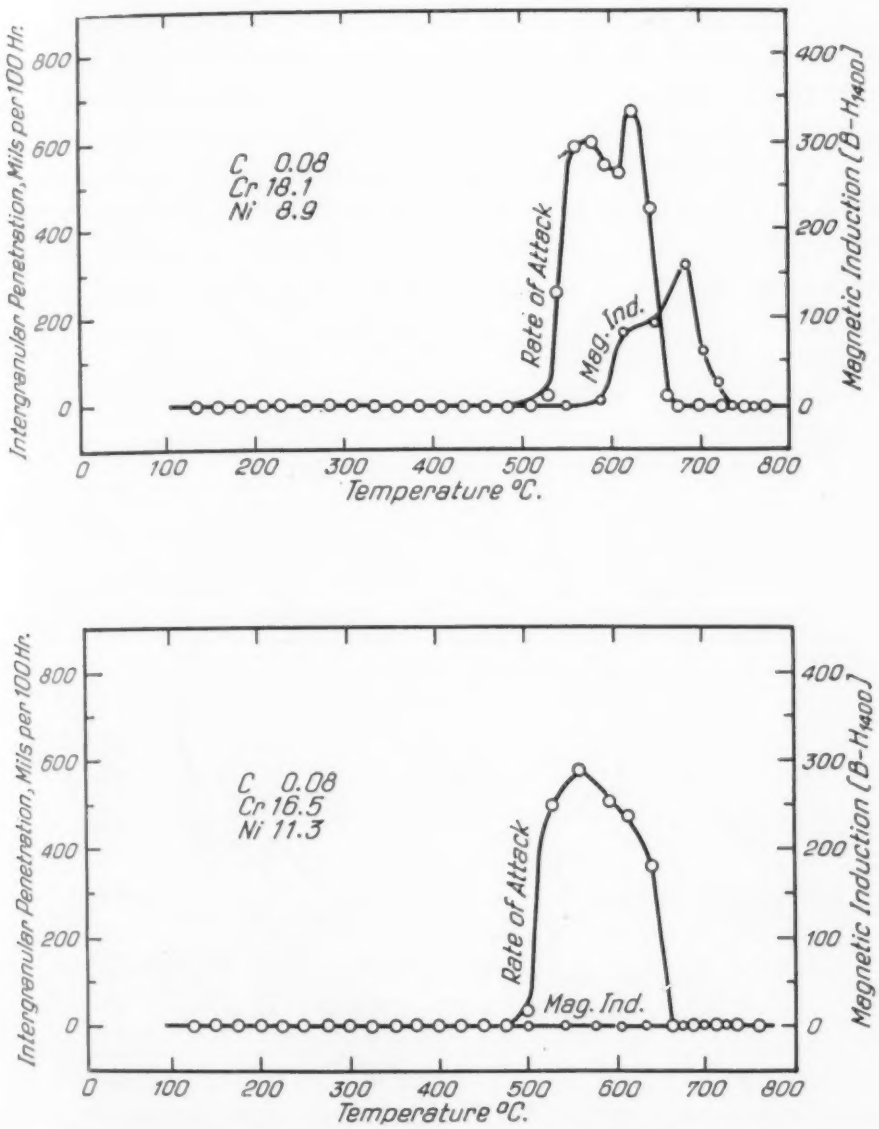


Fig. 7—Comparison of an 18-8 and 18-12 Alloy with Respect to Coincidence of Sensitization and Development of Magnetic Induction. In the Former the Magnetic Effect Appears at Higher Temperatures than Sensitization and the Latter Shows no Magnetic Change after the 1000 Hours Heating.

nickel content reduces the proportion of magnetic material produced without diminishing materially the susceptibility to intergranular corrosion.

Microscopic Appearance of Sensitized Material—A typical 18-8 alloy, as described in publications on metallography, is merely a uniform solid solution, the grains of which are all of the same single constituent. Carbon is dissolved in the alloy in accord with the solu-

bility curve of Fig. 8. A moderately rapid cooling retains the carbon which had dissolved at higher temperatures, and, accordingly, photomicrographs of the typical material usually appear with no metallic constituents other than the austenite solid solution. When, however, an alloy containing over about 0.03 per cent carbon is heated in the temperature range in the vicinity of 1200 degrees Fahr. (650 degrees Cent.), a new phase in the form of minute particles makes its appearance at the grain boundaries. This is well illustrated

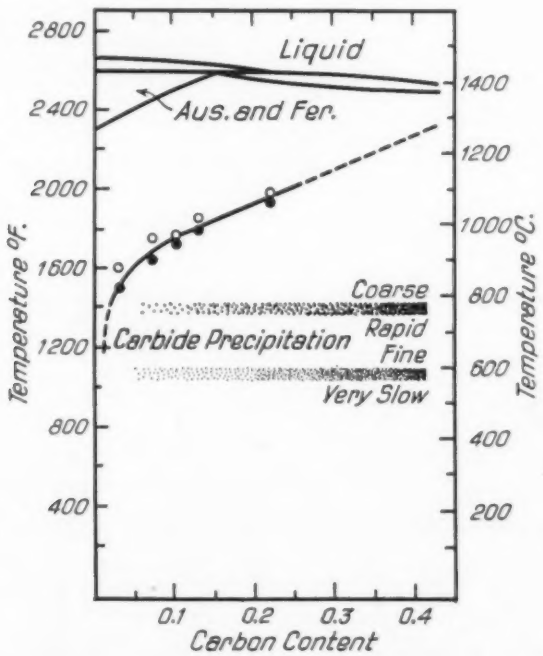


Fig. 8—Approximate Carbon Solubility in 18-8 Alloy.

in the photomicrograph of Fig. 9. Such metal is, in general, susceptible to intergranular attack. Reheating to temperatures above that at which the carbon completely dissolves, in accord with Fig. 8, removes the dark-etching precipitate at the grain boundaries, and a test shows complete restoration of properties. The apparent volume of the precipitate under comparable conditions varies with the total carbon and reaches zero at about 0.02 per cent carbon; the inference has been drawn that it is carbide which is responsible for the grain boundary alteration upon intermediate heating. That no other compounds are rejected at the grain boundaries could scarcely be inferred, but the evidence is strong that the grain boundary precipitation is dominantly a matter of carbon behavior.

Spontaneous Partial Recovery—It has been observed (Fig. 3) that while a short precipitation period at certain temperatures may cause high susceptibility, a longer time interval at the same temperature may effect some improvement in the alloy with respect to intergranular attack. In general this secondary phenomenon is accompanied by an increase in the average size of the carbide particles, and diffusion of carbon must, therefore, have occurred; the total volume

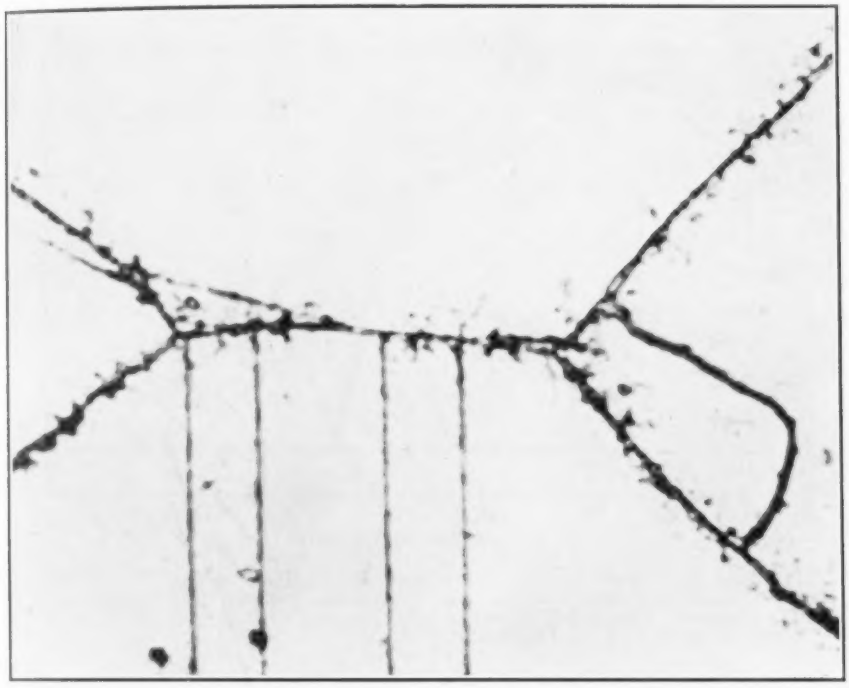


Fig. 9—Photomicrograph of Carbide Particles Precipitated in Grain Boundaries. × 3000.

of the carbide has increased and the susceptibility has decreased. A plausible hypothesis for the whole mechanism should have due regard for this circumstance. In addition, the partial recovery of fine-grained material is more rapid and more complete than that of the very coarse. It is not unusual to find no susceptibility to specific intergranular attack in an alloy containing, for example, 0.10 per cent carbon after heating for 1000 hours at 1290 degrees Fahr. (700 degrees Cent.), in which, however, there are numerous large carbide particles of some 0.0005 millimeter in diameter, aggregating, perhaps, 1 per cent of the volume of the alloy. On the other hand, severe susceptibility often results from the precipitation of an almost negligible proportion of the carbon as carbide. Clearly, then, sensiti-

zation does not depend upon the actual mass of precipitated phase.

Extent of Susceptible Paths—Some information may be gleaned from the actual loss of weight attending the complete disintegration of a specimen in the sensitized condition. In an average case some two per cent of the total specimen weight is lost in the copper sulphate-sulphuric acid sensitivity test. The greatest weight of carbide (of any suggested composition) which can possibly be developed in such a specimen is about 1.25 per cent, and accordingly the inter-

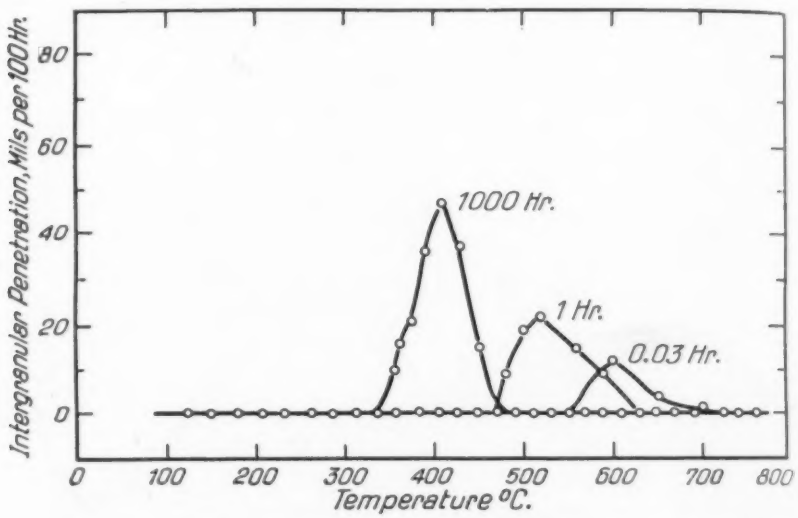


Fig. 10—Sensitivity, in Cold-worked Alloy, Measured as Penetration in 100-hour Corrosive Attack, after 2 Minutes, 1 Hour, and 1000 Hours at a Series of Constant Temperatures. Compare with Fig. 2, Same Alloy Not Cold-worked; Note Difference in Scale.

granular attack has removed much more than the carbide particles—indeed, it may be questioned whether they are removed at all except mechanically. A fairly wide swath has been cut along the grain boundaries through solution of the matrix itself. From this circumstance alone it may be inferred that a serious change has occurred in the metal itself near the grain boundaries.

Influence of Sensitization upon Mechanical Properties—Austenitic stainless steel in which carbide precipitation has occurred offers no exception to the general rule that the formation of particles of a new phase in a metal increases its strength and reduces its plasticity. 18-8 metal, for example, which has been sensitized by heating in the range 1000 to about 1400 degrees Fahr. (550 to 750 degrees Cent.) gains slightly in strength and suffers a small loss in reduction of area, elongation, and impact strength. Table II indicates that a

Table II

Effect of Prolonged Periods of Sensitization on Mechanical Properties at Room Temperature

Nominal Chemical Composition, %		Time Hours	Temperature Fahr.	Tensile Strength Pounds per Square Inch	Per Cent Elong. 2 In.	Charpy Impact ft.-lb.	Izod Impact ft.-lb.
Carbon	0.07	1000	900	.....	..	82.5	..
Manganese	0.5	1000	1250	.....	..	57.5	..
Silicon	0.5	1000	1370	.....	..	63.0	..
Nickel	8.0	1000	1450	.....	..	42.0	..
Chromium	18.0	1000	1650	.....	..	51.0	..
		1000	1750	.....	..	67.0	..
		0	1110	92,600	60	24.2 m.kg. per sq. cm.	..
		10	1110	.....	..	21.8 m.kg. per sq. cm.	..
		300	1110	94,800	56	20.8 m.kg. per sq. cm.	..
		0	1290	92,600	60	24.2 m.kg. per sq. cm.	..
Carbon	0.12	10	1290	.....	..	20.4 m.kg. per sq. cm.	..
Nickel	8.6						
Chromium	18.0	300	1290	103,500	47	12.3 m.kg. per sq. cm.	..
		0	1470	92,600	60	24.2 m.kg. per sq. cm.	..
		10	1470	.....	..	18.3 m.kg. per sq. cm.	..
		300	1470	98,600	50	3.7 m.kg. per sq. cm.	..
		1	1000	.....	..	.....	112
		1971	1000	.....	..	.....	107
Carbon	0.07	1	1200	.....	..	.....	113
Nickel	8.0	2059	1200	.....	..	.....	104
Chromium	18.0	3068	1200	.....	..	.....	105
		1	1550	.....	..	.....	112
		2307	1550	.....	..	.....	94
		3316	1550	.....	..	.....	121
		1	1000	.....	..	.....	112
		1971	1000	.....	..	.....	106
		1	1200	.....	..	.....	109
Carbon	0.11	2059	1200	.....	..	.....	43
Nickel	8.0	3068	1200	.....	..	.....	30
Chromium	18.0	1	1550	.....	..	.....	112
		2307	1550	.....	..	.....	55
		3316	1550	.....	..	.....	63

definite, though not alarming, loss of valuable properties occurs. (All properties measured at room temperature.)

The values shown in Table II[6] refer to metal in the sensitive state, but no opportunity was provided for intergranular attack to develop, except possibly by air oxidation. Obviously, if the heating is carried out in the presence of corrosive gases, then some actual intergranular penetration may occur and the physical properties suffer as a result. It should be recognized that a decrease in Charpy impact strength from about 80 to 40 foot-pounds still leaves the

[6]Data collected in A. S. T. M. Symposium, 1931. "Effect of Temperature on Properties of Metals," p. 482.

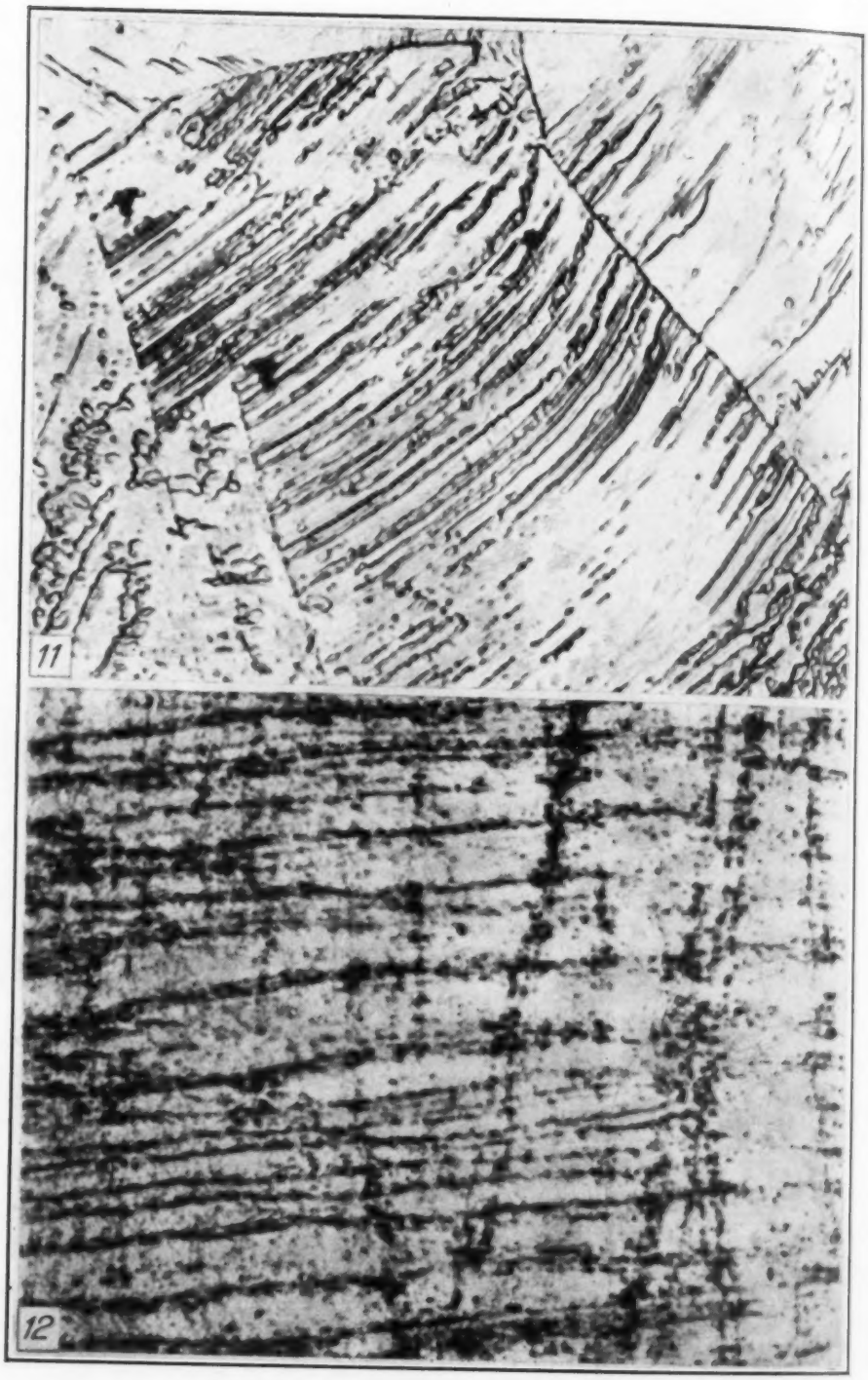


Fig. 11—Slip Bands in Cold-worked 18-8 Alloy. × 2000.
Fig. 12—General Carbide Precipitation upon Slip Planes Within the Grain. × 2000.

metal in a relatively highly ductile condition. Furthermore, it is observed that after heating for thousands of hours at 1300 degrees Fahr. (700 degrees Cent.), the metal often completely recovers its full intergranular corrosion resistance while the impact strength is definitely reduced. The loss of ductility and intergranular sensitization both accompany carbide precipitation but have, otherwise, no fundamental inter-relation.

Influence of Deformation—The effect of prior cold deformation upon the sensitization of the austenitic stainless steels is of major importance. Indeed, the subject might, perhaps, have been assigned a full chapter without very great over-emphasis. Strictly speaking, deformation exerts an influence on several of the characteristics already discussed but in the interest of simplicity it will be discussed merely as one of the series of factors influencing intergranular corrosion. Fig. 10 shows the penetration of corrosion as estimated from increase in electrical resistance in a cold-worked 18-8 material of 0.08 per cent carbon content, after 2 minutes, 1 hour, and 1000 hours at a series of constant temperatures. This chart should be compared with other similar charts for annealed metal, e.g., Fig. 2. It is quite apparent that the material has been greatly fortified by the deformation against the sensitizing effect of intermediate heating. More noteworthy is the remarkably rapid recovery of resistance to intergranular penetration by continued heating at the temperature which at first induced sensitivity. At a temperature of about 1100 degrees Fahr. (600 degrees Cent.) maximum sensitivity is developed in about 2 or 3 minutes, while in about ten hours a complete recovery is realized. This metal has been deformed by a reduction in cross section of 50 per cent.

Deformation proceeds in the austenitic stainless steels, as in all metals, by the mechanism of slip along crystal planes. Such slip planes in 18-8 metal are unusually clearly visible in the microscope, as in Fig. 11. The prominence of the slip bands may be due to the circumstance that deformation causes transformation of the austenite to ferrite (or perhaps it should be designated "low-carbon, high-alloy martensite") in these alloys in amounts which decrease with increase in the nickel and carbon content. Presumably, the bands have actual width and consist of transformed metal. The important point is that, upon heating, carbide precipitates upon every slip band nearly as readily as upon the original grain boundaries. The photomicrograph of Fig. 12 shows the carbide precipitation upon slip

planes and it will be observed that an almost general rejection of carbide has occurred instead of the strictly intergranular distribution. The profound effect of this circumstance will be further discussed under the heading "Mechanism of Sensitization."

Influence of High-temperature Ferrite—When the usual austenitic stainless steels of the 18-8 type are heated in the vicinity of 2400 degrees Fahr. (1300 degrees Cent.) or above, some pools of ferrite are developed; the amount decreases with increase of nickel or carbon. Silicon, molybdenum, tungsten, vanadium, chromium, titanium, or aluminum, when in solution, increases the proportion of this insular ferrite either as formed by heating or as remaining from the original ingot or billet structure. Whenever there is some appreciable amount of this ferrite a slight change in the mode of carbide precipitation occurs. The boundaries of the austenite grains in the immediate vicinity of the ferrite masses do not reject carbide so rapidly as usual; instead the ferrite pool itself seems to contain most of the carbide particles. But these ferrite grains do not suffer as severe sensitization as the austenite through precipitation. Probably the ferrite regions are much richer in chromium than the austenite itself. At any rate, when an austenitic stainless steel contains a fair proportion of high-temperature ferrite its sensitization is distinctly reduced and retarded, although not to an entirely dependable extent. Much of the effect of tungsten and molybdenum is probably due to the ferrite-forming tendencies of these elements, quite as much as to their carbide-forming capacities.

Summary of Characteristics

1. The susceptibility to the specific intergranular corrosion to which austenitic stainless steel is subject increases in severity with continued heating at a temperature in the intermediate range; it reaches a maximum and then with further heating begins to lessen. At the low sensitizing temperatures this recovery may not begin in less than thousands of hours and is, therefore, not ordinarily observable. At the higher temperatures the recovery may begin in a few hours or less.

2. The severity of the sensitization is proportional to the carbon content of the alloy with little regard to the content of chromium and nickel within the normal limits for the 18-8 or 18-12 alloys.

3. Coarse-grained material is sensitized more rapidly than finer grained metal.

4. Alloys of the ordinary 18-8 compositions develop some small amount of ferrite and, therefore, become magnetic with sensitization. The maximum magnetic induction does not coincide with maximum sensitivity and higher nickel alloys become sensitive without becoming magnetic.

5. An intergranular precipitation of a phase, almost certainly carbide, clearly visible in the microscope as very fine particles, typifies the sensitive metal.

6. The actual intergranular corrosion involves a relatively wide pathway through the metal along the grain boundaries. The carbide particles are probably not dissolved, but the portion of the grain near the grain boundary appears to vanish.

7. The plasticity of the 18-8 alloy is somewhat reduced with sensitization and its hardness and strength increase.

8. Cold-worked metal is more rapidly sensitized, but ultimately never so severely as the annealed, and it promptly begins to be restored with further heating. In this case carbide separation occurs on all slip planes substantially as effectively as upon grain boundaries, giving the effect of a general rather than localized precipitation.

9. In two-constituent alloys, carrying ferrite pools, carbide rejection shows a preference for the ferrite regions which do not show the sensitization imparted to the purely austenitic alloys. The presence of ferrite, therefore, usually reduces sensitization.

The Mechanism of Sensitization

The observations upon metal during and after sensitization detailed above permit a possible reconstruction of the mechanism somewhat as follows:

Upon heating the uniform supersaturated solid solution of carbon (e.g., 0.10 per cent) in the austenitic alloy, a temperature is reached at which sufficient diffusion of carbon may occur to permit the formation of carbide particles. It is a very important habit of carbide in austenitic stainless steel to form almost wholly at the grain boundaries in the early stages of precipitation. This building of minute crystallites of carbide seems to have a practically zero rate at temperatures below about 710 degrees Fahr. (375 degrees Cent.), but, even at slightly higher temperatures, carbide in appreciable quantity is formed in a few thousand hours, while as short an interval as 2 seconds at 1400 degrees Fahr. (760 degrees Cent.) will induce pre-

cipitation. Although they have not been measured, the size of the particles at early precipitation stages must be extremely small.

Larger particles of carbide in alloys carrying a high chromium content have been analyzed and found to contain some 90 per cent chromium. The plausible assumption is made that a high proportion of chromium is likewise combined in the very small particles of carbide precipitation at the early stages. Statistically, well over one-quarter of the atoms on every other plane in the solid solution are chromium atoms; on certain lines extending through the alloy every other atom is a chromium atom. In other words, no chromium atom (on the average) is separated from its nearest chromium neighbor by more than one iron atom, although a representative group of 1000 atoms of the 0.10 per cent carbon 18-8 alloy is comprised as follows:

Carbon	5 atoms
Nickel	75 atoms
Chromium	190 atoms
Iron, etc.	730 atoms

Hence, the building of a chromium-rich carbide crystallite is not difficult if the preference for carbon to combine with chromium instead of iron is marked, as, indeed, it is known to be. Conceivably, there may be some Fe_3C formed in the pre-sensitive stage, but it is believed that by the time precipitation is discernible by the microscope, the carbide is extremely high in chromium—possibly approaching Cr_4C.

Fig. 13 sets forth schematically the probable shift in chromium and carbon distribution in the region of a grain boundary when a crystallite of carbide forms. On the basis of its availability, carbon *must* migrate from a greater distance than chromium, otherwise no carbide nucleus could grow continuously. Accordingly, appreciable carbide may form by inducing chromium-depletion only in a very minute zone about the row of carbide particles. How great the depletion is can only be inferred, but in any event it must be severe, for a net chromium content in excess of about 11 or 12 per cent permits no attack. If chromium migration were much more rapid, the depleted zone would soon regain its proper allotment of chromium and, even perhaps at no time, fall below the reaction limit value.

Actually, after a relatively very long time, chromium does apparently diffuse into the previously impoverished zone from the more

than adequate store in the grains, with the attendant recovery of corrosion resistance in the grain boundary region. This state of affairs is represented in the charts of Fig. 14. Here, in the region within migration distance of the carbide particle, carbon is largely depleted, while chromium is again at a concentration above the attack

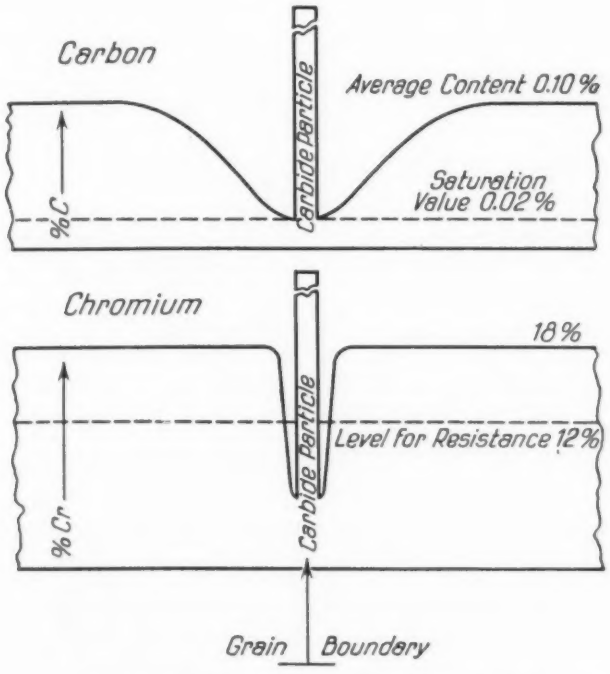


Fig. 13—Idealized Diagram Showing Probable Distribution of Carbon and Chromium Concentration (Ordinate) in the Vicinity of a Carbide Particle. Abscissa is Merely Distance on Either Side of the Grain Boundary.

limit. One may assume that diffusion does not occur when the concentration gradient falls below some minimum finite value.

It should be emphasized that this whole matter of intergranular attack hinges upon the single circumstance of the comparative lack of carbide precipitation nuclei in the body of the grain. For some reason, the relief of carbon supersaturation in austenitic stainless steel occurs almost wholly by grain boundary rejection. Some supersaturated solutions, e.g., all the useful age-hardening alloys, develop precipitation nuclei throughout the whole of the grain. A number of others are in the class with the stainless steel under discussion, which, instead of developing good age-hardening properties, shows chiefly a loss in ductility and little gain in hardness as the supersaturation is relieved by reheating (aging).

In a state of complete equilibrium at, for example, 1100 degrees Fahr. (600 degrees Cent.) one would find a typical 18-8 alloy consisting of carbide particles, containing some 90 per cent chromium, imbedded in a solid solution containing, uniformly at every point, about 0.025 per cent carbon and about 16.8 per cent chromium instead of 18 per cent. Such a structure would not be sensitive. It

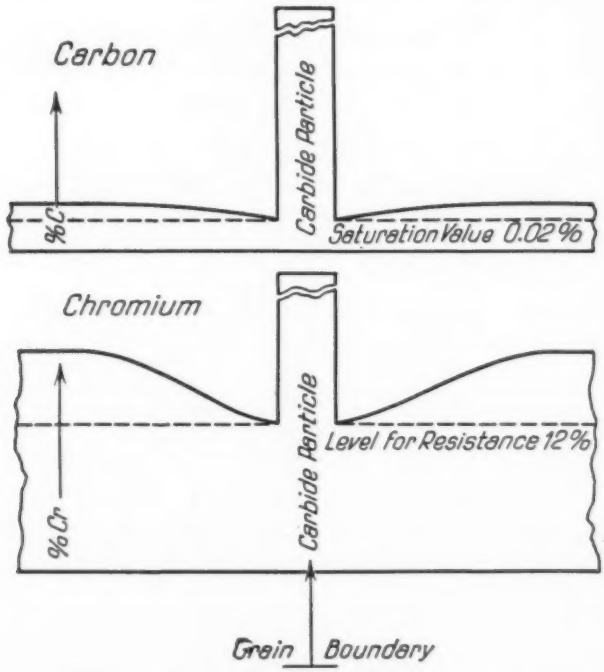


Fig. 14—Idealized Diagram, for Comparison with Fig. 13, Showing Carbon and Chromium Distribution after Sufficient Approach to Equilibration to Restore Grain Boundary Corrosion Resistance.

is then the failure to reach complete equilibration which is responsible for chromium depletion. Any factor which accelerates the final approach to equilibrium will likewise hasten the spontaneous recovery of the alloy.

Turning attention to the rapid recovery of intergranular resistance in the cold-worked alloy, it will become evident that actual equilibration is rendered possible by the ubiquity of slip bands upon which carbide may precipitate. The carbon is quickly exhausted by the general precipitation throughout the grains and at no point, therefore, has the chromium content been very greatly reduced. Diffusion, although relatively slow, is ample to transport chromium over the very short distances involved and, furthermore, the equilibration process is thus not frustrated by further combination of chromium

and carbon. In brief, cold work induces the regular age-hardening state of affairs to obtain, in a material which otherwise fails to provide precipitation nuclei except at grain boundaries.

In any event, it appears that the characteristic intergranular deterioration is adequately explained by chromium impoverishment; and that the assumption of the removal of carbon from a wide zone about the grain boundary and of chromium from only a narrow zone, accounts for the subsequent spontaneous partial or complete restoration of the alloy.

Prevention of Intergranular Corrosion

At the outset it will be apparent that the reduction of the carbon content to the solubility limit (approximately 0.02 per cent) at temperatures below 1000 degrees Fahr. (540 degrees Cent.) would eliminate sensitization altogether, but such a course is impractical at present. Two distinct methods are available, however, for accomplishing this end.

Cold Work Equilibration—This first has already been touched upon under the heading, "Influence of Deformation." The spontaneous recovery discussed therein is quite clearly a means of preventing a further heating at intermediate temperature from inducing the sensitive condition. With the employment of a very long period of heating the equilibration of the alloy may be accomplished at the very temperature of subsequent heating, which might otherwise have sensitized the metal, but temperatures slightly higher may be safely used with the saving of much time. In ordinary annealed metal the period for spontaneous recovery is impracticably long when the desensitizing temperature is sufficiently near the temperature of subsequent heating. On the other hand, the restoration of cold-worked metal proceeds with satisfactory velocity at temperatures even as low as 1290 degrees Fahr. (700 degrees Cent.) and the subsequent heating is without appreciable effect. Desensitization at temperatures in excess of 1380 degrees Fahr. (750 degrees Cent.), while very rapid, permits the retention of sufficient carbon in solution to permit slight sensitization with a subsequent long time heating, as in service, at 1000 degrees Fahr. (540 degrees Cent.), and is, therefore, not to be recommended. An attempt at desensitization at temperatures which cause full recrystallization may fall short, since subsequent precipitation of carbon in solution would again be driven to the grain boundaries.

Titanium—The method of preventing the development of intergranular susceptibility to attack in the austenitic stainless steels at present most widely in use is the addition of a small, appropriate amount of titanium in the metallic state. The degree of improvement brought about by the addition of titanium can be inferred from the results of a 1000-hour comparative heating test, covering a temperature range from 400 to 1600 degrees Fahr. (200 to 870 degrees

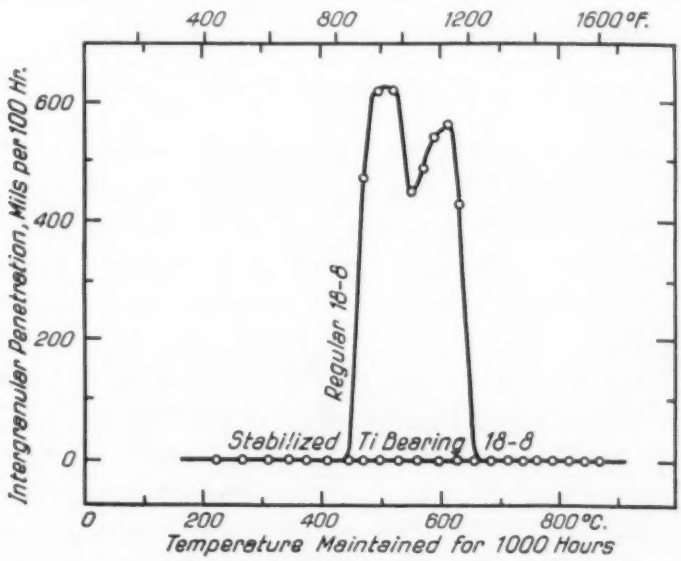


Fig. 15—Comparison of Titanium-bearing and Regular Annealed 18-8 with Respect to Sensitization in 1000 Hours at a Series of Constant Temperatures.

Cent.). The comparison alloy, an ordinary 18-8 material of almost identical analysis, except with respect to titanium, was rendered extremely susceptible to attack, while, as may be seen in the chart of Fig. 15, the titanium-bearing alloy was not measurably affected. The intergranular corrosion test in the standard copper sulphate-sulphuric acid solution, even when prolonged to 1000 hours, had no measurable effect upon the titanium-bearing alloy; the ordinary material heated in the temperature range 950 to 1100 degrees Fahr. (500 to 600 degrees Cent.) disintegrated to a powder in less than 10 hours. The high sensitivity of this testing method leaves little doubt of the efficacy of titanium in eliminating this shortcoming of the austenitic stainless steels.

In the use of titanium, it is important that this element be introduced, without simultaneous addition of carbon, in such a manner as to insure its preservation in the metallic state, because, as will be out-

Table III

Mechanical Properties of a Typical Stabilized Titanium-bearing 18-8 Alloy

Form	Ultimate Strength Pounds per Square Inch	Yield Point Pounds per Square Inch	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area	Rockwell "B" Hardness
16 gage sheet	95,000	37,200	55	..	82
Seamless tube	91,000	47,000	56	54	83

Analysis

Carbon	Nickel	Chromium	Titanium
0.07	9.12	18.08	0.38

lined below, its efficacy depends upon its combining power with carbon. A sufficient proportion must be present, and this proportion has been experimentally determined as approximately 6 times the carbon content in excess of 0.02 per cent. The basis for this rule will be developed below. Moreover, the alloy must be so treated,

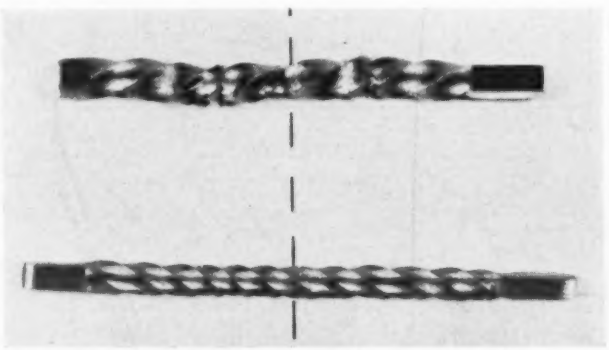


Fig. 16—Photograph of Welds, Regular and Titanium-bearing 18-8, both Subjected to Corrosive Solution and Twisted. Note Cracks in Regular Material.

prior to final fabrication, that opportunity is provided for the titanium to accomplish its purpose. The titanium-bearing alloy, so treated, is hereafter designated as "stabilized."

When these requirements have been met the alloy may be welded without regard to a subsequent heat treatment. In titanium-bearing metal, properly manufactured, the familiar zones on either side of a weld, distinctly susceptible in ordinary 18-8, as may be seen in Fig. 16, are not marked by any measurable susceptibility. In material held at the most destructive temperature for 1000 hours, the susceptibility is reduced by titanium in the order of 10,000 to 1, as measured in terms of penetration by the electrical resistance method.

Table III sets forth the mechanical properties of typical stabilized titanium-bearing 18-8 metal.

In titanium-bearing alloys carbide precipitation does occur, although of a vastly different nature from that in ordinary metal. Accordingly, heating in the intermediate temperature range may cause some change in physical properties; the tensile strength is increased

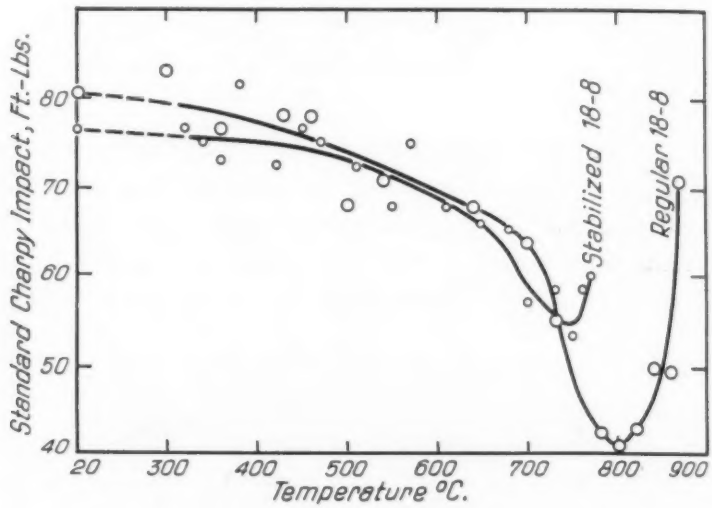


Fig. 17—Impact Strength of Stabilized Titanium-bearing and Regular 18-8 after 1000 Hours Exposure to Series of Constant Temperatures as Plotted Along Abscissa.

and the impact strength is somewhat reduced. Due to the extreme plasticity of the austenitic alloy these changes still leave the material in a class with the toughest metals. The result of 1000 hours heating, at various constant temperatures, upon the impact strength of the titanium stabilized alloy in comparison with ordinary 18-8 metal is shown in Fig. 17.

The addition of titanium to 18-8 metal, in excess of the recommended ratio, serves to provide a certain margin of safety in metal which has been much over-heated prior to exposure to temperatures which would sensitize ordinary metal. This is usually entirely unnecessary and tends in the extreme case to develop ferrite in the otherwise austenitic alloy, a circumstance contributing magnetic induction and a small change in mechanical properties. There is little gained by high titanium ratio and at the same time there are no significant disadvantages, except in special cases. If ferrite is disadvantageous, higher nickel may be employed to eliminate it.

The Mechanism of Titanium Stabilization

The explanation offered above, for the development of susceptibility in the austenitic stainless steels, assigns the principal role to chromium-rich carbide, with attendant local chromium impoverishment. It is believed that the function of titanium is to usurp for itself the power of carbide formation, leaving the chromium free to remain in solid solution, where it contributes its full measure of cor-

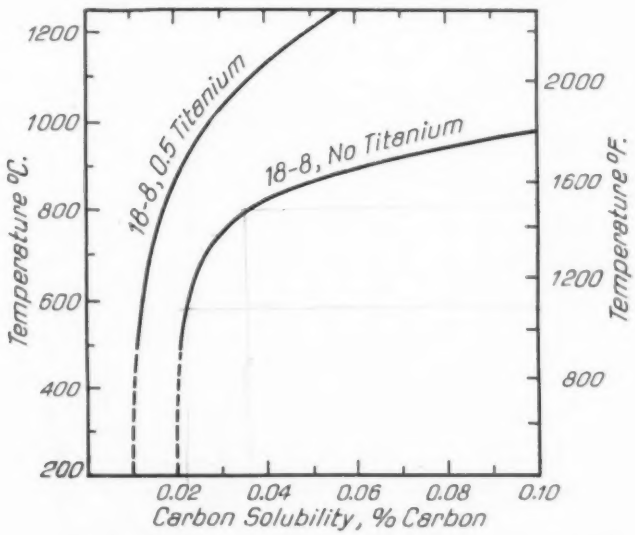


Fig. 18—Comparison of Carbon Solubility in Regular and in Titanium-bearing 18-8 Alloy.

rosion resistance. Evidence is not lacking which points to a carbide-forming activity on the part of titanium far in excess of that of chromium; certainly titanium carbide is a very stable compound and it is not difficult to believe that at equilibrium the carbon of an alloy would be largely combined with titanium unless the quantity of titanium was insufficient. Some small amount of each would still remain in solution even if the concentration were in correct proportion to form the carbide TiC, but this amount must be exceedingly small. Excess of titanium would still further reduce the carbon not so combined. In solids, as contrasted with liquids, equilibrium is usually only slowly reached at moderate temperature and the reactions actually observed depend as much upon the particular *rates* at which possible combination and diffusion may occur as upon the conditions imposed at equilibrium. At very high temperatures, at which diffusion is relatively rapid, solids may behave somewhat as do

most liquids, and the analogy certainly holds for the reduced solubility of the carbon in the presence of an element such as titanium with which it combines preferentially. Thus, it is believed that carbon solubility in an 18-8 alloy is shifted, as in Fig. 18, by the presence of approximately 0.5 per cent titanium.

With respect to carbon combination, it appears that substantial equilibrium is reached in a few minutes at temperatures above per-

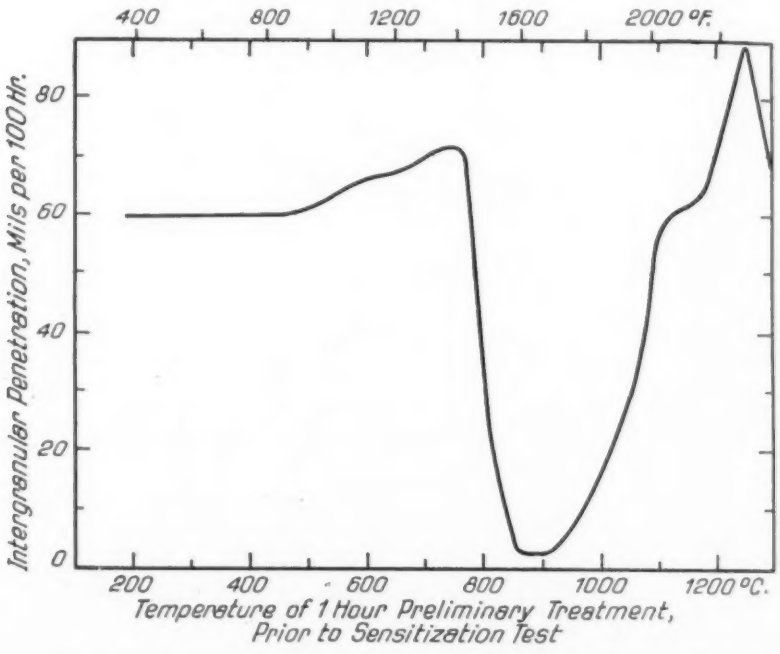


Fig. 19—Degree of Sensitization as Affected by 1 Hour Preliminary Heating. Test to Develop Susceptibility Consists of 100 Hours at 1100 Degrees Fahr. (600 Degrees Cent.). Note Efficacy of 1 Hour at about 1600 Degrees Fahr. (870 Degrees Cent.).

haps 1825 degrees Fahr. (1000 degrees Cent.), but at lower temperatures reactions are increasingly slow, so that the constitution of the alloy at equilibrium is not readily approached; indeed, it appears that reactions may occur which are not at all in line with the ultimate equilibration. A fairly large section of titanium-bearing metal rejects the carbide of titanium upon slow free cooling in accord with the carbon solubility for a time, but below some temperature, perhaps not far from 1825 degrees Fahr. (1000 degrees Cent.), the carbon is not able to withdraw from solution and therefore remains in a supersaturated solution. It might be expected that a prolonged heating at say 1000 degrees Fahr. (540 degrees Cent.) would result in the establishment of equilibrium for that temperature through

the precipitation of titanium carbide; but in 18-8 alloys containing well over the probable combining (stoichiometric) proportion of titanium, a really significant, though small, amount of chromium carbide is formed. Under such conditions of experiment a sensitization may actually be detected. The explanation for this circumstance appears to involve the contemplation of relative-diffusion probabilities.

In a 0.5 per cent titanium alloy a representative group of 1000 atoms will contain—

Titanium	6 atoms
Carbon	5 atoms
Nickel	75 atoms
Chromium	190 atoms
Iron, etc.	724 atoms

Each carbon atom has only to find one titanium atom for combination to form TiC, but must associate with it four chromium atoms for the building of a crystallite of Cr_4C; but there are 190 chromium atoms for each 6 of titanium and the purely statistical probability for forming Cr_4C as against TiC is therefore 190/4:6 or about 8:1. Hence, on the basis of availability of atoms the urge to equilibrium (TiC versus Cr_4C) must overcome odds of 8:1; at elevated temperature where diffusion is easy, equilibrium is reached, but at lower temperatures, where diffusion is retarded, and paths of diffusion are lengthened by previous combinations, the carbon is well content to form a small amount of chromium carbide.

However, it will be seen that the carbon concentration at the solubility limit in the 0.5 per cent titanium alloy is, at about 1650 degrees Fahr. (900 degrees Cent.), already not in excess of that at which chromium carbide may form at even as low a temperature as 1000 degrees Fahr. (540 degrees Cent.); hence, if approximate equilibrium may be induced at this temperature, or a little below, then no sensitization will later develop. Fortunately, a quite practical heating for a period of 2-4 hours at 1560 degrees Fahr. (850 degrees Cent.) accomplishes complete immunization of the alloy and this is the customary procedure employed in preparing the titanium-bearing material for use involving heating at intermediate temperatures.

The effectiveness of this simple handling of titanium-bearing metal is illustrated in Fig. 19. The metal was heated for 100 hours at 1100 degrees Fahr. (600 degrees Cent.) for sensitization, following a one-hour heating at the various temperatures of the abscissa.

The severity of attack on the metal to which this sensitizing treatment was applied for test reaches substantially zero for all material previously equilibrated in 1 hour at a temperature between 1560 and 1650 degrees Fahr. (850 and 900 degrees Cent.).

The conclusion as to the desirable proportion of titanium to incorporate into the 18-8 alloy is drawn from a comparatively simple practical test of a number of alloys containing a variety of carbon

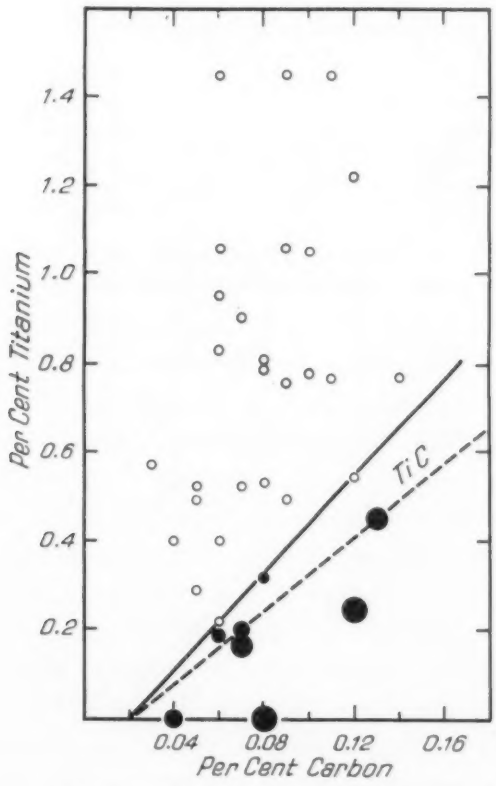


Fig. 20—Determination of Requisite Ratio, Titanium to Carbon, for Stabilization. Open Circles Indicate no Attack, Size of Solid Circles Denotes Relative Degree of Penetration.

and titanium concentrations. All the materials were coarsened at about 2010 degrees Fahr. (1100 degrees Cent.) to predispose rapid sensitization and then sensitized at 1200 degrees Fahr. (650 degrees Cent.) for 16 hours. Intergranular corrosion was brought about in the sensitized members of the series by the customary immersion in boiling sulphuric acid-copper sulphate solution for 24 hours. Even slight intergranular attack was made evident by a twisting operation and the results are shown graphically in Fig. 20. Compositions

showing no detectable attack are designated as open circles; the relative intensity of attack in the others is indicated by the size of the solid circles. A line marking the approximate boundary between susceptible and nonsusceptible compositions is drawn. Since the slope of this line is about 5.5 and since the prolongation of the line indicates that about 0.02 per cent carbon causes no susceptibility in titanium-free alloys, a general working rule for determining the minimum content of titanium which should be present in the alloy is as follows: subtract 0.02 from the carbon percentage, and multiply by 6.

Clearly, the exact maximum carbon content for actual freedom from possible sensitization in titanium-free alloys is not determined in this test and it may lie at a value slightly below 0.02 carbon—but for commercial material the validity of this rule is not affected by this circumstance.

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12. Added Note: The following French Patents relating to this general subject have just come to the authors' attention: 667843, 682455, 717664, 720008, and 742004, all except the last issued to Fried. Krupp A. G.

BEHAVIOR OF STEEL IN SULPHUR-CONTAINING ATMOSPHERES AT FORGING TEMPERATURES

By D. W. Murphy

Abstract

The results of an investigation at forging temperatures of the effect of adding small amounts of sulphur dioxide and hydrogen sulphide to the products of combustion of city gas and air on the scaling losses, sulphur content and structure of the steel are presented. Sulphur dioxide is shown to affect the steel very powerfully, increasing the sulphur content of the outer layers of steel and the scaling losses tremendously, while hydrogen sulphide employed under proper conditions is not so intense in its action. These effects increase with increasing temperature, increasing time and increasing percentage of sulphur dioxide. The ability of the atmosphere to form oxides is shown to be a powerful factor in aiding the diffusion of sulphur in steel. Of the various kinds of steels subjected to atmospheres containing sulphur dioxide, those containing nickel were found to be more adversely affected than either plain carbon or chromium steels.

THIS paper is based on part of the investigation on scaling conducted during the past three years at the University of Michigan for the Committee on Industrial Gas Research of the American Gas Association. This particular part of the research program was concerned with determining the effects of small amounts of sulphur gases on steel at forging temperatures. In some fuels, sulphur occurs to the extent of one to two per cent. This quantity of sulphur will, under most conditions of burning, yield, in the products of combustion forming the furnace atmosphere, 0.1 to 0.2 per cent of sulphur gases. Since the most important sulphur gases which are likely to be met in forging furnace atmospheres are sulphur dioxide and hydrogen sulphide, the work has been limited to the study of additions of these two gases.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author is a member of the society and is research associate, Department of Engineering Research, University of Michigan, Ann Arbor, Michigan. Manuscript received June 17, 1932.

Literature

The literature pertaining to the action of sulphur gases on steel is not extensive and much of the work has been done below 1800 degrees Fahr. (980 degrees Cent.) in connection with special corrosion and heat-resistant steels. Campbell[1] established the fact that sulphur could diffuse rapidly in the presence of oxygen. H. J. French[2] reported that, at 900 degrees Fahr. (480 degrees Cent.) in atmospheres containing hydrogen sulphide, increasing chromium decreased the sulphur attack while nickel increased it. This conclusion has been substantiated by subsequent researches. Hatfield[3] called attention to the increased scaling losses in atmospheres containing sulphur dioxide at 1650 degrees Fahr. (900 degrees Cent.) in comparison with scaling losses in similar atmospheres containing no sulphur dioxide. Several authors,[4] participating in a symposium of the American Petroleum Institute on corrosion, discussed experiments showing that hydrogen sulphide or sulphur vapor were the chief offenders in corrosion of oil-cracking units.

Gruber[5] studied the effects of sulphur gases on a number of steels in the temperature range from 1290 to 1830 degrees Fahr. (700 to 1000 degrees Cent.). His results indicated that the presence of nickel decreased the resistance to sulphur attack, while chromium and aluminum were somewhat beneficial. This work also demonstrated the increasing seriousness of sulphur attack as temperature is increased. Gruber also gave typical photomicrographs showing the nodule formation with hydrogen sulphide and the intercrystalline penetration with sulphur dioxide. Gruber and Wellman[6] agree that hydrogen sulphide is more active toward steels at these temperatures than is sulphur dioxide. The poor resistance of nickel-containing steels as well as the activity of hydrogen sulphide seems to be well substantiated in the work of these authors.

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[4]W. G. Whitman and J. K. Roberts, R. L. Duff and C. Retailliau and F. R. Lang, *Proceedings*, American Petroleum Institute, Vol. 11, 1930, p. 150-63.

[5]H. Gruber, Zeit. fur Metallkunde, Vol. 23, 1931, p. 151.

[6]E. Wellman, Zeit. Elektrochem. Vol. 37, 1931, p. 142.

It will be noted that none of these data indicate the effects of sulphur gases on steel at forging temperatures. From the results of low temperature studies, it might be expected, however, that the attack would be more severe at these higher temperatures.

Method

The methods used in the study reported in this paper differed somewhat, especially in the stripping process, from those employed in the previous investigations on scaling reported in a series of papers by Jominy and Murphy[7] and by Murphy, Wood and Jominy[8]. A gas-fired muffle furnace, having a 2-inch porcelain tube projecting through it, was used for heating. The city gas, air, and sulphur dioxide or hydrogen sulphide were introduced at the back of the furnace. Samples of gases for analysis were withdrawn in the front. Sulphur gases were determined by an iodimetric process suggested by Dennis in which the gases are drawn through a given quantity of standard iodine solution until the iodine solution is completely used. The percentage of sulphur gas is then calculated from the two quantities, the total volume of gas used and the volume of the sulphur gas corresponding to the quantity of standard iodine solution. Other constituents of the combustion products were determined in a modified Orsat apparatus.

The analyses of the steels used are given in Table I. The samples were placed in the porcelain tube and heated for a chosen period of time under various conditions of temperature and atmosphere. At the end of the heating period the samples were withdrawn from the furnace into a quenching bath of distilled water to remove some scale and stop the reaction. It was found to be impossible to use an electrolytic stripping cell for removing the remaining scale because much of the sulphur in the outer layers of metal was removed and lost as hydrogen sulphide during the stripping action. It was consequently necessary to remove the scale by mechanical means which, of course, diminished the accuracy of the determination of scaling losses.

After mechanical cleaning, the samples were turned to furnish chips for sulphur analyses at various depths. One end of each sample

[7]W. E. Jominy and D. W. Murphy, Transactions, American Society for Steel Treating, Vol. 18, 1931, p. 19.

[8]D. W. Murphy, W. P. Wood, and W. E. Jominy, Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 193.

Table I

Chemical Composition of the Steels

Per Cent

Steel	Carbon	Manganese	Silicon	Sulphur	Phosphorus	Nickel	Chromium	Vanadium	Molybdenum	Tungsten
1015	0.19	0.53	0.18	0.020	0.016	....	....	....	....	....
1030	0.28	0.653	0.01	0.032	0.013	....	....	....	....	....
1050	0.52	0.64	....	0.034	0.025	....	....	....	....	....
1090	0.88	0.34	....	0.018	0.029	....	....	....	....	....
2320	0.17	0.59	0.24	0.020	0.018	3.40	....	....	....	....
3130	0.35	0.56	....	0.025	0.016	1.11	0.56	....	....	....
6145	0.47	0.58	0.16	0.015	0.015	....	0.98	0.24	....	....
4140	0.39	0.67	....	0.024	0.020	....	0.93	....	0.32	....
4615	0.21	0.54	0.29	0.012	0.017	1.81	....	....	0.25	....
High Speed	0.73	0.32	0.08	0.018	0.025	....	4.27	1.06	....	18.62
Nitralloy	0.35	0.45	0.30 max.	0.025 max.	0.025 max.	....	1.25	....	0.20	1.00 Al

was always preserved for microscopic examination. Sulphur analyses were also made of all scales to complete the record and furnish additional light on the mechanism of sulphur effects.

The results of the research are presented in this paper under three divisions: the first pertaining to atmospheres containing sulphur dioxide, the second to those containing hydrogen sulphide, and the third to the influence which oxygen has on both scaling losses and the penetration of the sulphur.

Atmospheres Containing Small Amounts of Sulphur Dioxide

The variables considered in connection with the study of the effects of atmospheres containing small amounts of sulphur dioxide on scaling losses, on sulphur content of steel and scale, and on the structure of steel were: the percentage of sulphur dioxide, temperature, time, type of atmosphere, and composition of steel.

Variation of Percentage of Sulphur Dioxide

The results obtained when the percentage of sulphur dioxide was varied are shown graphically in Fig. 1. The tests were carried out at 2300 degrees Fahr. (1260 degrees Cent.) for 40 minutes with city gas and air so proportioned as to give practically complete combustion, since under these conditions of atmosphere sulphur dioxide was known to be stable. Scaling losses apparently increase very rapidly as the quantity of sulphur dioxide is increased to about 0.2 per cent. Larger amounts of sulphur dioxide further increase scaling losses,

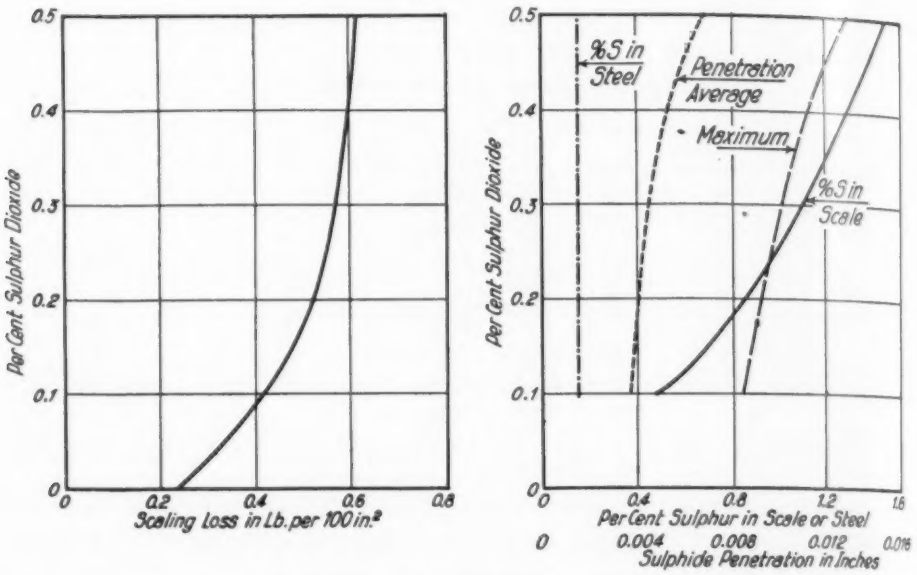


Fig. 1—Effect of Variation of Per Cent Sulphur Dioxide. Atmosphere, complete combustion of city gas and air. Temperature, 2300 Degrees Fahr. (1260 Degrees Cent.). Time, 40 minutes.

but not so rapidly as was the case below 0.2 per cent. With 0.1 to 0.5 per cent sulphur dioxide present, the scaling losses are 1.8 to 2.6 times the losses in atmospheres containing no sulphur dioxide.

The percentage of sulphur in the outer 0.01 inch of steel apparently does not vary greatly with the amount of sulphur dioxide present in the atmosphere since it remains practically constant at about 0.16 per cent. The original sulphur content of this S. A. E. 1015 steel was 0.02 per cent. The sulphur in the outer layers of metal after exposure is thus increased about eight times the original amount. The sulphur content of the scale increases quite consistently from about 0.45 per cent with 0.1 per cent sulphur dioxide to 1.5 per cent with 0.5 per cent sulphur dioxide. Both average and maximum penetrations of sulphides into the steel increase with increasing amounts of sulphur dioxide. In Fig. 4, which shows the structure of the outer layers of metal, there is a clearly marked attack around the austenitic grain boundaries. This accounts for the large difference between maximum and average penetration.

Variation of Temperature

The graphical summary in Fig. 2 of the results obtained when temperature of exposure was varied bears evidence that scaling losses

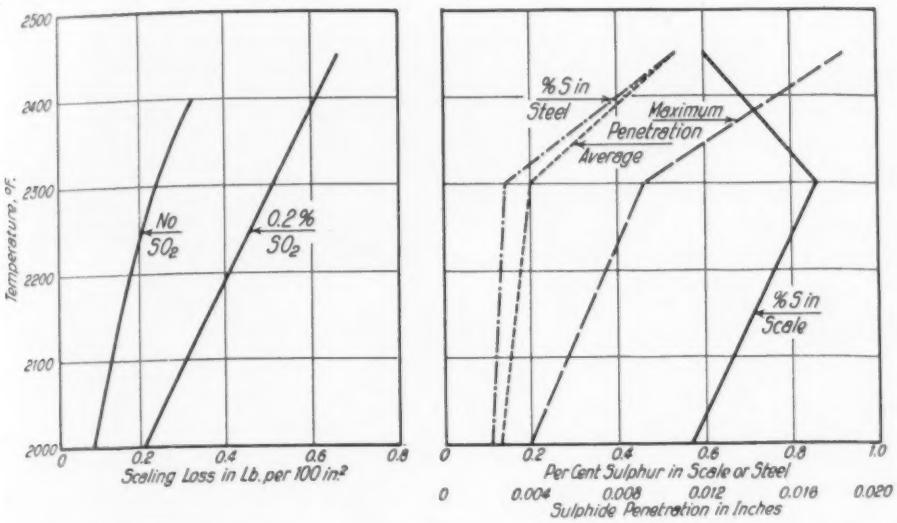


Fig. 2—Effect of Variation of Temperature. Atmosphere, complete combustion of city gas and air. Time, 40 minutes. Sulphur dioxide, 0.2 per cent.

of S. A. E. 1015 steel increase more rapidly with increasing temperature with sulphur-bearing atmospheres than is the case with atmospheres containing no sulphur. The sulphur content of the outer layer of metal increases somewhat from 2000 to 2300 degrees Fahr. (1095 to 1260 degrees Cent.), but above this temperature the sulphur content increases enormously, attaining a value of 0.54 per cent at 2450 degrees Fahr. (1345 degrees Cent.), 27 times the amount initially present. The sulphur content of the scale increases up to 2300 degrees Fahr. (1260 degrees Cent.) and then decreases sharply with further raising of the temperature. Evidently the diffusion of sulphur into the steel has become sufficiently rapid to prevent the building up of the sulphur content of the scale.

The average and maximum penetrations of sulphides likewise have their sharpest increase above 2300 degrees Fahr. (1260 degrees Cent.), which points to markedly increased rates of diffusion in steel above 2300 degrees Fahr. In Figs. 3, 4, and 5 are shown the structures of steel heated at 2000, 2300, and 2450 degrees Fahr. (1095, 1260 and 1345 degrees Cent.). At 2450 degrees Fahr. (1345 degrees Cent.) the attack is very severe, much more so, in fact, than that at 2300 degrees Fahr. (1260 degrees Cent.), Fig. 4. At 2000 degrees Fahr. (1095 degrees Cent.) the inclusions seem to be chiefly sulphides, while at higher temperature they consist of oxide-sulphide complexes. The oxide-sulphide combination seems to have a much more rapid rate of diffusion than either the oxide or sulphide.

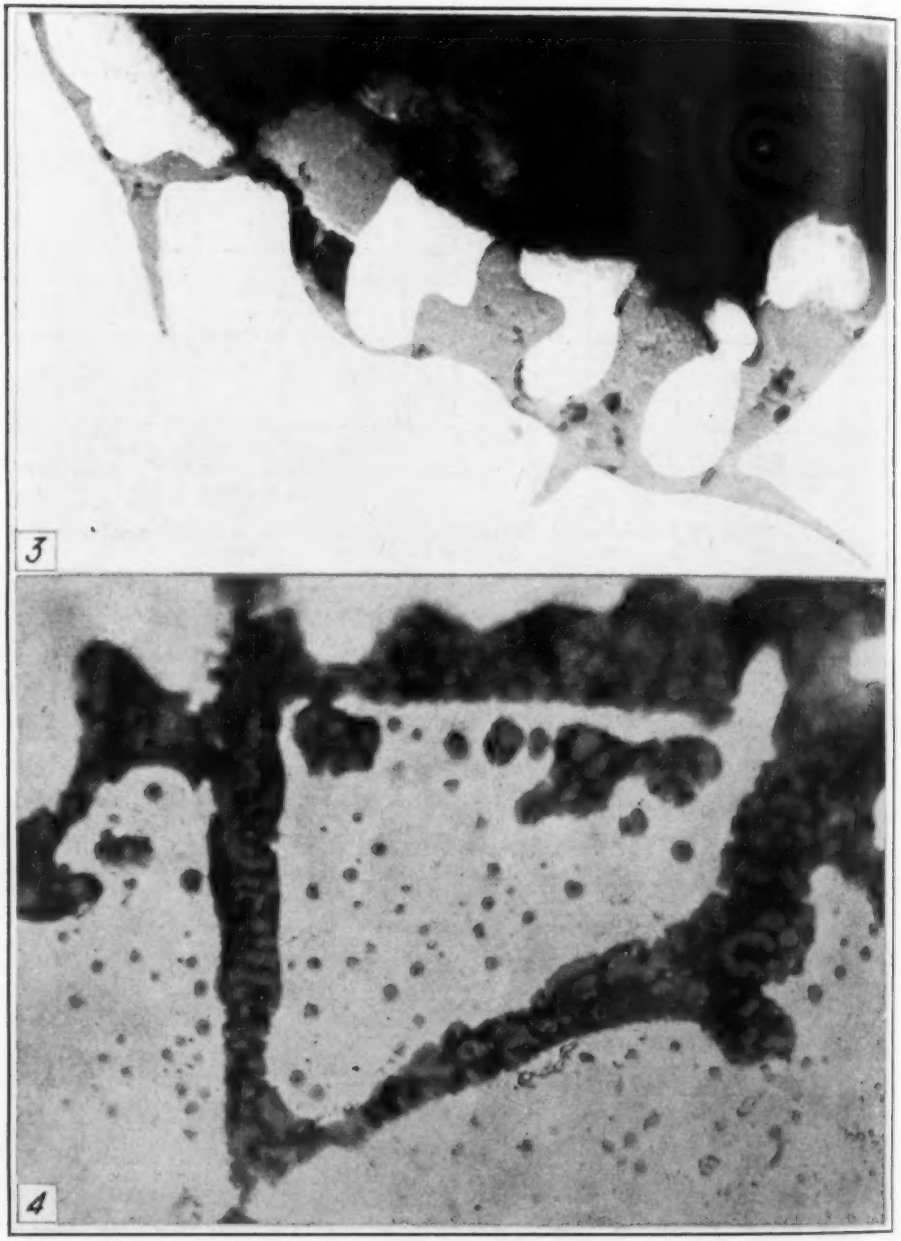


Fig. 3—S.A.E. 1015 Steel, Heated at 2000 Degrees Fahr. (1095 degrees Cent.), 60 Minutes. 0.2 per cent SO_2; complete combustion of city gas and air. × 500. Unetched.

Fig. 4—S.A.E. 1015 Steel, Heated at 2300 Degrees Fahr. (1260 Degrees Cent.), 40 Minutes. This Photomicrograph Shows Clearly the Different Character of the Inclusions formed at 2300 Degrees Fahr., when Compared with those Formed at 2000 Degrees Fahr. (1095 Degrees Cent.). The Oxide-sulphide Eutectic is very Apparent. × 750. Unetched.

Variation of Time

The curves of Fig. 6 make it evident that the scaling losses, the penetration of sulphides, and the sulphur content of the steel, increase with increasing time of exposure to products of combustion of city gas and air containing 0.2 per cent sulphur dioxide at 2300 degrees Fahr. (1260 degrees Cent.). The linear form of the curve for the effect of variation of time on scaling losses suggests at once that the scale formed on steel in sulphur dioxide-bearing atmospheres offers no protection against further scaling. In atmospheres containing no sulphur dioxide scaling occurs at a decreasing rate as time is increased. This effect of sulphur dioxide atmospheres is probably due to the fact that the oxide-sulphide type of scale formed possesses a low melting point, probably in the vicinity of 2000 degrees Fahr. (1095 degrees Cent.) or lower. A scale that is at least partly liquid has been found to have practically no effect in reducing the rate of scaling.

Inasmuch as the mechanism of penetration of sulphur into steel is essentially one of diffusion, it would be expected that the sulphur content of the steel and the penetration of sulphides as shown by the microscope would increase with increasing time. The curves of Fig. 6 confirm this assumption. The curve for maximum penetration indicates that the penetration of sulphides occurs at the rate of 0.01 inch per hour. Figs. 7 and 8, photomicrographs of runs of 40 and 120 minutes duration, show the effect of time on penetration. Fig. 8, for the 120-minute test, shows a better defined and deeper intercrystalline attack even at low magnification than is shown for the shorter test run in Fig. 7.

Variation of Type of Atmosphere

The data obtained when 0.2 per cent sulphur dioxide was added to various gas-air combustion atmospheres ranging from those containing excess oxygen to those containing excess carbon monoxide, are summarized in the curves of Fig. 9. For purposes of comparison, the scaling-loss curve for atmospheres containing no sulphur dioxide is plotted with that for atmospheres containing sulphur dioxide. The presence of 0.2 per cent of sulphur dioxide doubles the scaling losses of S. A. E. 1015 steel in atmospheres containing small amounts of oxygen or carbon monoxide. The effect of sulphur dioxide, however, decreases rapidly when the carbon monoxide content is increased

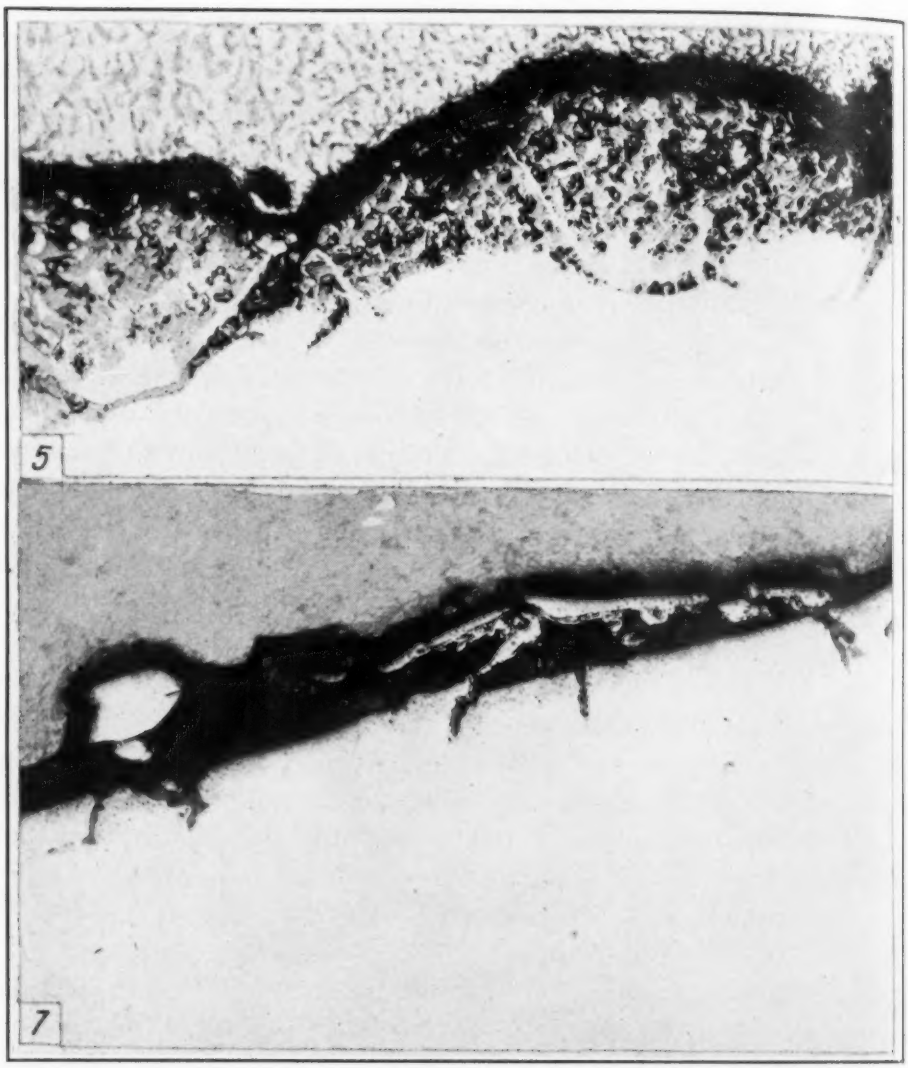


Fig. 5—S.A.E. 1015 Steel, Heated 40 Minutes in Atmosphere of Complete Combustion of City Gas-Air Mixture Containing 0.2 Per Cent SO_2 at 2450 Degrees Fahr. (1345 Degrees Cent.). Note the Severe Attack of the Steel by the Sulphur-bearing Atmosphere at the Higher Temperature. Unetched. × 100.

Fig. 7—S.A.E. 1015 Steel, Heated at 2300 Degrees Fahr. (1260 Degrees Cent.) for 40 Minutes in an Atmosphere of Complete Combustion of a City Gas-Air Mixture Containing 0.2 Per Cent SO_2. Note That There are many Globular Inclusions at the Edge Between the Cell Wall Type. Unetched. × 100.

because of its conversion to hydrogen sulphide. The crossing of these two curves may be attributed to the fact that the fuel gas in the two cases was quite different in composition and consequently resulted in combustion products whose carbon dioxide and water vapor content differed considerably. This, of course, affected the amount of scale produced.

Table II

Effect of Sulphur Dioxide on Scaling Losses and Sulphur Content of Plain Carbon and Alloy Steels. Time 40 Minutes. Temperature 2300 Degrees Fahr. Sulphur Dioxide 0.2 Per Cent. Atmosphere—City Gas and Air-Complete Combustion

Run No.	S.A.E. No.	Depth of Outer Layer (in.)	% S in Outer Layer	% S at Center	% S in Scale	Penetration of Sulphides (in.) Ave.	Penetration of Sulphides (in.) Max.	Scaling Loss in Lbs. per 100 in.²	Scaling Loss of Same Steel in Sulphur-Free Atmosphere Lbs./100 sq. in.
671	1015	0.012	0.110	0.019	0.855			0.516	0.237
672	1015	0.011	0.147	0.020	0.875	0.0040	0.0092	0.525	
A1-1	1030	0.009	0.069	0.026	0.384	0.0043	0.0081	0.182	0.324
A1-2	1030	0.012	0.063	0.027	0.322			0.251	
A2-3	1050	0.011	0.145	0.036	1.438			0.467	0.293
A2-4	1050	0.016	0.168	0.038	1.639	0.0035	0.0042	0.506	
A3-3	1090	0.015	0.133	0.020	1.318	0.0061	0.0083	0.477	0.179
A3-4	1090	0.015	0.184	0.016	1.670			0.521	
FF-1	2320	0.011	1.669	0.023	0.464	0.0131	0.0212	0.250	0.181
FF-2	2320	0.016	2.118	0.015	0.485			0.254	
GG-1	3130	0.016	1.270	0.020	1.332	0,0171	0.0355	0.330	0.185
GG-2	3130	0.019	1.043	0.018	1.201			0.311	
L-1	4615	0.012	1.772	0.022	0.998	0.0209	0.0292	0.275	0.172
L-18	4615	0.011	1.515	0.026	0.978			0.271	
KK-18	4140	0.018	0.384	0.034	1.499			0.258	0.260
KK-181	4140	0.012	0.428	0.032	1.524	0.0042	0.0050	0.387	
Q-1	6145	0.011	0.233	0.015	1.323			0.625	0.250
Q-3	6145	0.011	0.169	0.014	1.315	0.0030	0.0050	0.600	
YY-18	High Speed	0.011	0.391	0.035	0.995	0.0042	0.0042	0.326	0.371
X-2	Nitralloy	.....	0.107	0.024	3.42	0.0039	0.0059	0.433	.....

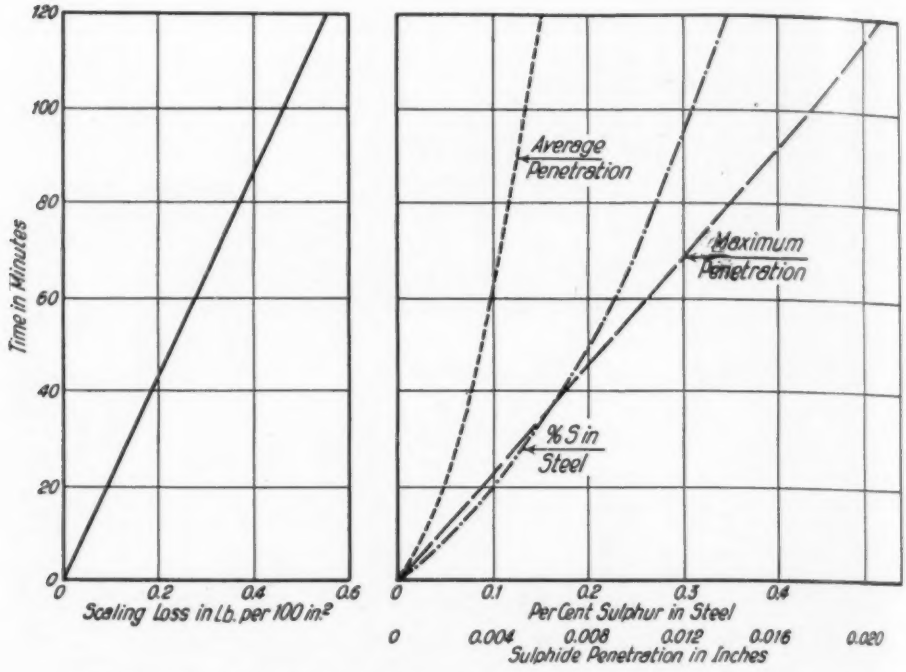


Fig. 6—Effect of Variation of Time. Atmosphere, Complete Combustion of City Gas and Air. Temperature, 2000 Degrees Fahr. (1095 Degrees Cent.). Sulphur Dioxide, 0.2 per cent.

The amount of sulphur introduced into the outer layer of the steel decreases from about 0.25 per cent at 2.0 per cent oxygen to about 0.10 per cent at 12.0 per cent carbon monoxide. Likewise, the penetration decreases rapidly as the atmospheres are varied from those containing 2.0 per cent oxygen to those containing 12.0 per cent carbon monoxide. On the other hand, the sulphur present in the scale increases rapidly with increasing carbon monoxide content of the atmosphere. These facts indicate that the presence of considerable oxygen in the form of oxides is necessary for the rapid diffusion of sulphur into steel. Since the amount of oxides formed is decreased by increasing the carbon monoxide content, the diffusion of sulphur is increasingly hindered.

Effect of Atmospheres Containing Sulphur Dioxide on Different Steels

In Table II are summarized the results of exposing various types of steel to the products of complete combustion of city gas and air containing 0.2 per cent sulphur dioxide. Among the plain carbon steels practically no differences are apparent in the effects of sulphur-bearing atmospheres on scaling losses, penetration of sulphide, or

sulphur content of the outer layers of metal. The case of alloy steels is different. The sulphur content of the outer layer of steel shows tremendous variations. It is particularly high, over 1.0 per cent, in steels containing nickel, and considerably less, below 0.4 per cent, in steels containing chromium without nickel. The penetration of sulphides is likewise much greater in the case of nickel steels than in the case of those containing no nickel. The sulphur content of the scale, however, shows no marked differences. The scaling losses are, for the most part, higher in sulphur-bearing atmospheres than in those containing no sulphur. In general, nickel steels are most adversely affected by sulphur-containing atmospheres. Fig. 10 shows an S. A. E. 2320 steel heated in a sulphur-bearing atmosphere at 2300 degrees Fahr. (1260 degrees Cent.). The violent attack is readily apparent; in fact it is extremely difficult to say where scale stops and metal begins, for there are many small grains of steel apparently included in the oxide-sulphide mass. This difficulty may account in part for the high sulphur contents obtained on the outer layers of nickel steels.

Atmospheres Containing Small Amounts of Hydrogen Sulphide

Hydrogen sulphide is stable in gas-air combustion atmospheres only in the presence of large amounts of hydrogen and carbon monoxide. For this reason most of the tests were made in an atmosphere containing about 12 per cent carbon monoxide with at least as much hydrogen. The results obtained when the percentage of hydrogen sulphide, temperature, and time were varied are presented in Tables III and IV.

Variation of the Percentage of Hydrogen Sulphide

Varying the amount of hydrogen sulphide from 0.1 to 0.2 per cent as indicated in Table III produces no marked effect on scaling losses. This is explained by the fact that the gas atmosphere is nearly non-scaling to steel so that only very small amounts of scale would be formed. The sulphur content of the scale shows a decided increase as the amount of hydrogen sulphide is increased, which parallels the effect found in the case of sulphur dioxide. This result is to be expected since increasing the amount of sulphur in the gas increases the amount available to form sulphides.

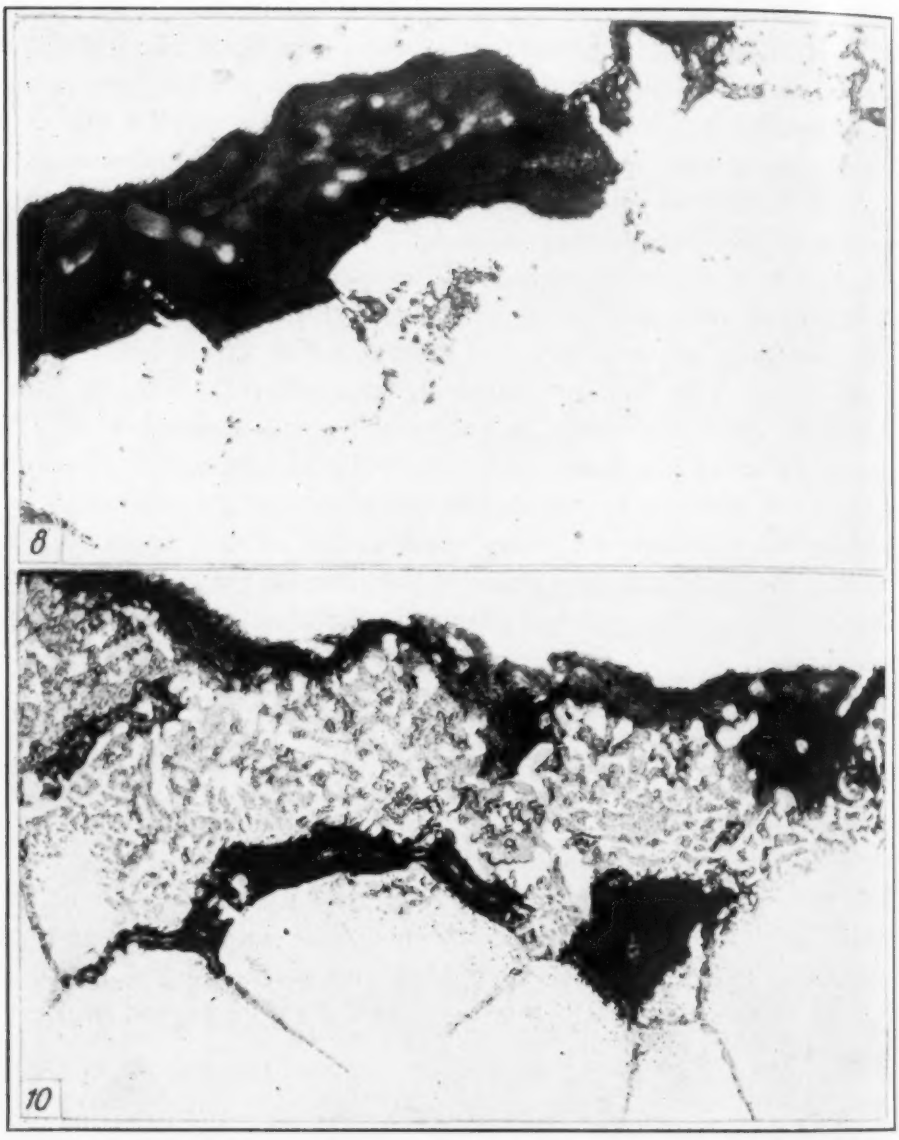


Fig. 8—S.A.E. 1015 Steel, Heated at 2300 Degrees Fahr. (1260 Degrees Cent.) 120 Minutes, 0.2 Per Cent SO_2 Complete Combustion of City Gas-Air Mixture. Compare the Penetration of Inclusions in this Run at 2300 Degrees Fahr. (1260 Degrees Cent.) with that in Fig. 7, Run Under Similar Conditions Except that the Time was 40 Minutes.

Fig. 10—S.A.E. 2320 Steel, Heated 40 Minutes in Atmosphere of Complete Combustion of a City Gas-Air Mixture Containing 0.2 Per Cent SO_2 at 2300 Degrees Fahr. (1260 Degrees Cent.). Note Severe Attack Sustained by Nickel-bearing Steel in Sulphur Atmosphere at Forging Temperatures. Unetched. × 100.

The sulphur content of the outer layer of steel is, of course, increased over its initial value in the unheated samples, but the increase is not as marked as in the case of the additions of sulphur dioxide. Furthermore, there is no distinct increase in the concentration of

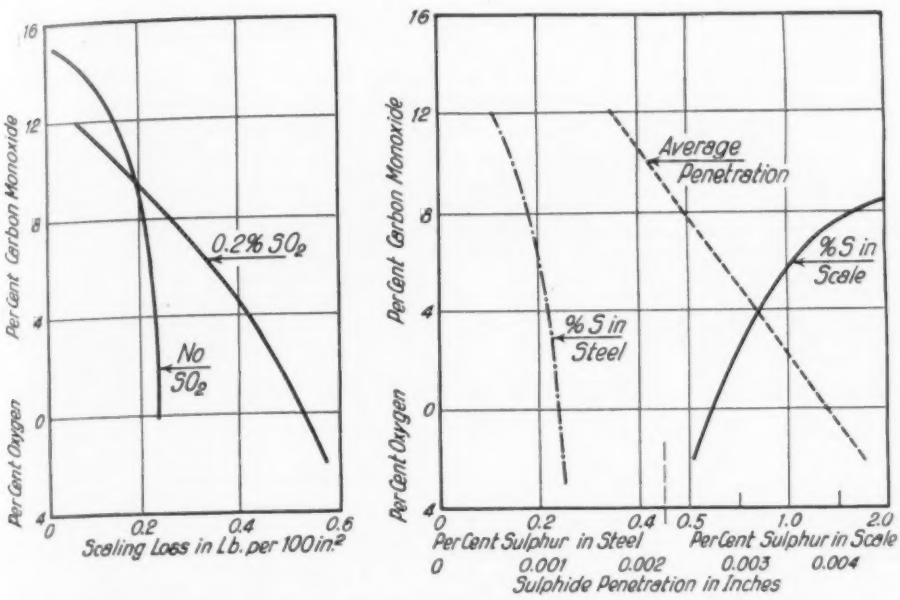


Fig. 9—Effect of Variation of Composition of Atmosphere. Temperature, 2300 Degrees Fahr. (1260 Degrees Cent.). Time, 40 minutes. Sulphur dioxide, 0.2 per cent.

sulphur in the outer layers of metal as the amount of hydrogen sulphide is increased. This fact is shown also in the figures for penetration of sulphides, for in all cases the penetration is low. It might also be pointed out here that there is a distinct similarity between these data for atmospheres containing 0.2 per cent hydrogen sulphide and 11.8 per cent carbon monoxide and the results obtained when 0.2 per cent sulphur dioxide was added to atmospheres containing 12.0 per cent carbon monoxide. This indicates that the sulphur is present in both cases as the same compound, which thermodynamic calculations show to be hydrogen sulphide which may, of course, be considerably dissociated into hydrogen and sulphur vapor. The structure of steel heated in atmospheres containing hydrogen sulphide is shown in Fig. 11. There is no intergranular penetration in this case, and, in addition, the inclusions formed in this treatment are of the sulphide type rather than of the oxide-sulphide type.

Variation of Temperature

The results given in Table III also indicate that there is little change in the activity of atmospheres containing hydrogen sulphide with increasing temperature. The scaling losses are almost totally unaffected, but the behavior of the sulphur content of the scale is

Table III

Effect of Varying the Per Cent of Hydrogen Sulphide and Temperature on the Sulphur Content and Scaling Losses of S. A. E. 1015 Steel
Atmosphere—City Gas and Air—Carbon Monoxide—11.8 Per Cent

Run No.	Temp. °F.	% H_2S	Depth of Outer Layer (in.)	% S in Outer Layer	% S at Center	% S in Scale	Penetration of Sulphides (in.) Ave.	Max.	Scaling Loss in Lbs./100 sq. in.
733	2000	0.1	0.011	0.060	0.020	0.964	0.00067		0.0398
734	2000	0.1	0.012	0.039	0.017	1.83			0.0328
738	2000	0.2	0.014	0.061	0.021	6.70	None		0.023
739	2000	0.2	0.012	0.058	0.022	9.70			0.016
732	2300	0.1	0.010	0.085	0.020	2.64	0.0013	0.0027	0.108
735	2300	0.1	0.007	0.042	0.019	3.80	0.0010	0.0027	0.011
736	2300	0.2	0.012	0.053	0.019	4.47			0.021
737	2300	0.2	0.010	0.060	0.020	5.03	0.0013	0.0032	0.016

Table IV

Effect of Variation of Time of Exposure and Temperature on the Sulphur Content and Scaling Losses of S. A. E. 1015 Steel
Hydrogen Sulphide 0.2 Per Cent. Carbon Monoxide 11.8 Per Cent

Run No.	Temp. °F.	Time (Min.)	Depth of Outer Layer (in.)	% S in Outer Layer	% S at Center	% S in Scale	Penetration of Sulphides (in.) Ave.	Max.	Scaling Loss in Lbs./100 sq. in.
742	2000	20	0.010	0.080	0.022	10.1	None		0.023
743	2000	20	0.013	0.058	0.021	11.5			0.013
738	2000	40	0.014	0.061	0.021	6.70	None		0.023
739	2000	40	0.012	0.058	0.022	9.70			0.016
740	2000	60	0.013	0.063	0.021	7.13	None		0.024
741	2000	60	0.017	0.067	0.024	9.16			0.022
746	2300	20	0.011	0.052	0.019	9.50	0.0016		0.021
747	2300	20	0.008	0.073	0.022	6.01			0.011
736	2300	40	0.012	0.053	0.019	4.47	0.0013	0.0032	0.021
737	2300	40	0.010	0.060	0.020	5.03			0.016
744	2300	60	0.012	0.070	0.022	5.89	0.0027		0.021
745	2300	60	0.011	0.066	0.019	5.38			0.016

quite anomalous. In the case of tests using 0.1 per cent hydrogen sulphide, there is an increase in sulphur content of the scale with increasing temperature, while in those using 0.2 per cent the sulphur content of the scale decreases with increasing temperature.

The sulphur content of the outer layer of metal shows only slight variations with temperature which could be entirely within the limits of experimental error. The penetration of sulphides is practically doubled by increasing the temperature from 2000 to 2300 degrees Fahr. (1095 to 1260 degrees Cent.), but, even so, the penetration is low. This probably indicates a considerable change in the solubility of sulphur in steel between 2000 and 2300 degrees Fahr. (1095 and 1260 degrees Cent.) since the solubility has an important effect in solid diffusion.

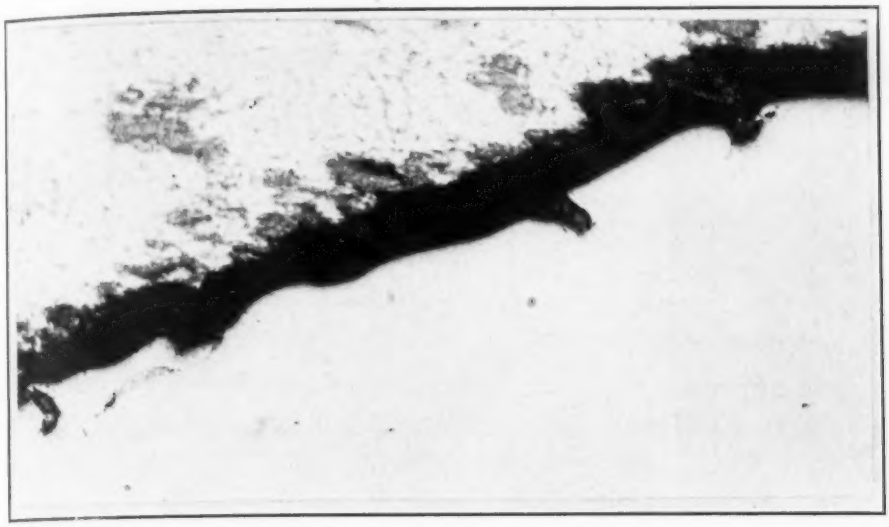


Fig. 11—S.A.E. 1015 Steel, Heated 40 Minutes in an Atmosphere From Combustion of a City Gas-Air Mixture Containing 8.0 Per Cent CO and 0.1 Per Cent H_2S, Temperature 2300 Degrees Fahr. (1260 Degrees Cent.). Note that Penetration of Inclusions is Much Less in Reducing Atmospheres. Unetched. × 100.

Variation of Time of Exposure

Table IV summarizes the data for variation of time of exposure to atmospheres containing 0.2 per cent hydrogen sulphide and 11.8 per cent carbon monoxide at 2300 degrees Fahr. (1260 degrees Cent.). The scaling losses are apparently very slightly affected by increasing time, which indicates that the atmosphere is nearly non-scaling to steel. There is some tendency for the sulphur content of the steel to increase with increasing time, but this is not as pronounced as in the case of sulphur dioxide tests. Accompanying the increase in sulphur content of the steel is a decrease in the sulphur content of the scale with increasing time. Finally the penetration of sulphides increases with increasing time, a result which is to be expected from the nature of the process of diffusion.

Variation of Type of Atmosphere

Fig. 12 shows a graphical summary of the data obtained when the carbon monoxide content of the atmosphere was varied from about 8 to 13.5 per cent keeping the hydrogen sulphide at 0.2 per cent. Scaling losses decrease decidedly with increasing carbon monoxide, as do the penetration of sulphides and the sulphur content of the steel. This behavior parallels that when sulphur dioxide was

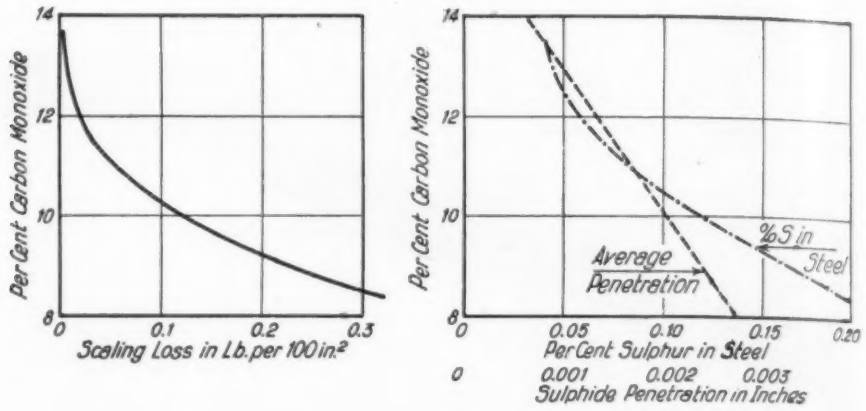


Fig. 12—Effect of Variation of Composition of Atmosphere. Temperature, 2300 Degrees Fahr. (1260 Degrees Cent.). Time, 40 Minutes. Hydrogen Sulphide, 0.2 per cent.

used under like conditions and suggests again that the sulphur is present in both cases in the same state. The curves in this figure emphasize further the fact that the ability of the atmosphere to form oxides as well as sulphides, which is the case in atmospheres low in carbon monoxide, is an important factor in determining the behavior of steel in sulphur containing atmospheres.

Influence of Oxygen on the Behavior of Steel in Sulphur-Bearing Atmospheres

Thus far it had been shown that sulphur dioxide is more powerful in its effect on steel than is hydrogen sulphide when each is used under conditions suiting its stability. It was apparent that the effect of sulphur dioxide in increasing scaling losses is associated with the formation of an oxide-sulphide eutectic which possesses a low melting point. This results in the formation of a scale which is at least partly liquid at the temperatures used in this research. Scaling, under such conditions, occurs at an approximately constant rate and is of course decidedly increased by increasing temperature.

It seemed desirable to determine also what influence oxygen has on the penetration of the steel by the sulphur. A series of special tests was, therefore, run on S. A. E. 1015 steel for this particular purpose. The results of these runs are summarized in Table V.

These runs clearly show that sulphur dioxide is much more powerful in its effect on steel than is either sulphur vapor or hy-

Table V

Special Runs at 2300 Degrees Fahr. (1260 Degrees Cent.)

Atmosphere	Penetration of Sulphides—Average (Inches)	Penetration of Sulphides—Maximum (Inches)	Sulphur Content Outer .01 Inch	Sulphur Content of Scale
1% H_2S; 99% N_2	0.001		0.07	3.27
0.5% SO_2; 99.5% N_2	0.0013	0.0027	0.115	11.40
S vapor + N_2	0.0005		outer 0.005 inches 0.25	

drogen sulphide. Since the only difference in atmospheres was that oxygen was available in the case of sulphur dioxide, it seems plausible to consider that oxygen intensifies the effects of sulphur on steel. It will be remembered that E. D. Campbell found oxygen to be a rather important factor in the diffusion of sulphur in steel. But apparently sulphur will diffuse without the assistance of a large supply of oxygen as the hydrogen sulphide and sulphur vapor runs indicate. The results of the foregoing table simply emphasize the fact which has been pointed out previously; that the ability of an atmosphere to form oxides as well as sulphides is important in determining its behavior with respect to steel.

It is quite probable that oxygen affects the diffusion of sulphur in steel by affecting the solubility of sulphides. Thus it might reasonably be postulated that oxide-sulphide complexes are more soluble in solid steel than either one alone, since with a greater solubility, a greater rate of diffusion might be expected. The rapid penetration of sulphur into nickel steels might likewise be considered to be due to some influence of nickel on the solubility of sulphur in steel.

Sulphur seems to penetrate steel in the case of atmospheres containing sulphur dioxide by way of the austenite grain boundaries and through the crystals themselves, while, in the case of atmospheres containing hydrogen sulphide, penetration is chiefly through the grains. Of the two types of penetration the intercrystalline type will of course lead to severe localized attacks, which accounts for the considerable differences in average and maximum penetrations in the case of atmospheres containing sulphur dioxide. Furthermore, this sulphur penetration has been shown to be increased by increasing the percentage of sulphur in the atmosphere, by increasing the time of exposure, and by increasing the temperature as is the case for all diffusional processes. In fact, temperature is a very powerful factor, since increasing the temperature increases the rate of diffusion to such an extent that the sulphur content of the scale is considerably

lowered. Many of the curves indicate that as the sulphur content of the scale, and consequently the sulphur gradient between scale and steel increases, the penetration of sulphur also increases. If, however, the oxygen supply is low, the establishing of high sulphur gradients between scale and steel apparently has no effect upon the penetration of sulphur into the steel. In this case, it would appear that the solubility of the sulphide is the determining and limiting factor.

Summary

This research has demonstrated the following conclusions:

1. Sulphur dioxide in combustion atmospheres increases scaling losses and introduces sulphur into the outer layers of metal.

2. Scaling losses and penetration of sulphides in atmospheres containing sulphur dioxide increase with increasing percentage of sulphur dioxide, with increasing temperature, and with increasing time.

3. Sulphur dioxide has a decreasing effect on scaling losses and penetration of sulphides as the carbon monoxide content of gas-air combustion atmospheres is increased. Sulphur dioxide has an increasing effect in atmospheres containing increasing amounts of free oxygen.

4. Hydrogen sulphide, when used under conditions suited to its stability, has less effect than sulphur dioxide on scaling losses and penetration of sulphides at forging temperatures. In general, the effects of increasing its percentage, the temperature, and the time of exposure are evident by the increasing penetration of sulphides.

5. When the carbon monoxide content of hydrogen sulphide containing gas-air combustion atmospheres is reduced, the effect of hydrogen sulphide on scaling losses and penetration of sulphides becomes similar to that of sulphur dioxide.

6. The use of high sulphur fuels, containing 1 to 2 per cent sulphur, in forging furnaces is likely to increase scaling losses and result in poorer forgings by reason of the sulphur introduced into the outer layers of the steel. Hence the sulphur content of fuels for use in forging furnaces should never exceed 0.5 per cent and should preferably be kept well below this figure.

7. Where ever high sulphur fuels are used, it is highly desirable to operate under strongly reducing conditions to prevent high sulphur contents in the outer layers of the steel.

8. Recognizing that little, if any, manufactured or natural gas

contains over 0.1 per cent sulphur, the precautions indicated in paragraphs 6 and 7 are of little moment when this type of fuel is used.

Acknowledgments

The author desires to express his appreciation to the Committee on Industrial Gas Research of the American Gas Association whose financial support enabled this study to be made. He also desires to acknowledge the aid of Messrs. M. G. Fontana, H. F. Bjork, J. E. Wilson, and R. Rodrian in conducting the many tests involved.

DISCUSSION

Written Discussion: By H. H. Ashdown, metallurgist, Westinghouse Electric and Manufacturng Co., East Pittsburgh.

I feel certain I am only voicing the feeling of indebtedness of all steel mill executives in expressing to the author a deep sense of appreciation for the valuable research work done in investigating furnace atmospheres and the cause of excessive scaling.

As already stated in my discussion on Dr. Murphy's paper on scaling during heat treatment, the direct and incidental losses to the steel manufacturer and engineer are far in excess of those computed.

Although I had for many years appreciated that scaling losses were greater when using inferior quality coal or gas from inferior coal, I had not before known or appreciated this was to a large extent due to the presence of sulphur dioxide and hydrogen sulphide. The thought had been that inferior fuel prolonged the heating period, resulting in increased scaling, and it was thought the resulting steel product might be somewhat inferior due to possible sulphur absorption.

The affinity of steel for sulphur at high temperatures has long been known, which carries my thoughts back some 20 years to Sheffield, England, where the staff of a certain steel plant, try as they would, could not produce steel of low sulphur content, or a steel of consistent sulphur content. This steel plant was comparatively near a chemical works and after considerable investigation it was noted with certain prevailing winds the steel was always of higher sulphur content, and on carefully checking up it was noted when certain directional winds blew across the chemical works toward the steel works, the steel was always higher in sulphur content. This may sound "fable-like," but is readily reasoned out when one considers the large volume of atmospheric air passing through the regenerators and over the steel bath during a period of about 12 hours. I remember also reading many years ago that good steel could not be made at the sea coast, due to the activity of ozone and consequent absorption of oxygen, and again the more rapid rate of oxidation in heating steels.

I do not know if there has actually been any work done along those lines in making a comparison of steels made under identical conditions along the coast and well inland, but in view of the great amount of research done in

recent years on oxygen contamination, this angle may be deserving of thought.

It appears that in a normal furnace atmosphere oxidation above 2000 degrees Fahr. takes place at a relatively greater rate than in a sulphur dioxide-enriched atmosphere; in the author's words, "when the temperature reaches 2300 degrees Fahr. the violent attack is readily apparent."

It is generally appreciated 2300 degrees Fahr. is a mellow soaking temperature, but under the now known conditions of rapid scaling, it may be found advisable to soak for a longer period at 2000 degrees Fahr. and for a relatively shorter time at 2300 degrees Fahr., unless it is found possible to effect a nonscaling atmosphere as indicated by the author. The important point is brought out that the presence of 11.8 per cent carbon monoxide slows down materially the rate of scaling and sulphur absorption.

The paper in itself in text, curves and tables, is so complete and definite that there is little room for questioning, but there is one point which to me is not altogether clear. In the experiments with hydrogen sulphide, the author on page 524 states that—"In the case of tests using 0.1 per cent hydrogen sulphide, there is an increase in the sulphur content of the scale, with increasing temperature, while in those using 0.2 per cent the sulphur content of the scale decreases with increasing temperature." By this, one has to assume at the higher temperature, a diffusion of the sulphur takes place. But on referring to the last item in Tables III and IV, at the higher temperature of 2300 degrees Fahr. the author shows a lower scale loss than at 2000 degrees Fahr. Is one to infer from this that during the diffusion of the sulphur a partial reduction of the oxide takes place simultaneously, yielding a lower scale percentage?

One potent phase brought out by this paper is the imperative selection of the highest quality fuel for heating steels intended for high duty work, particularly those selected for surface duty in service, such as case hardening and nitriding, and again the quenching steels, where the surface must be of the highest quality.

From the rapid rate of sulphur absorption at the maximum forging temperature and its known intercrystalline penetration, it is evident the finished steel surface would be high in sulphur content, which would not be revealed by normal methods of analysis.

If, as we have been led to believe in the past, the presence of sulphur in steel is exceedingly detrimental, every possible care should be taken to prevent its contamination. The author's present research was apparently based on this belief. Although not strictly relevant to this paper, I am raising another point of view on this same subject. Surely we are wanting in consistency and heading for danger when we add large quantities of sulphur or sulphur compounds to high quality steels to make them free cutting, and apparently much of this material is finding its way into high duty applications.

Written Discussion: By O. W. McMullan, metallurgical department, Timken-Detroit Axle Co., Detroit.

The author mentions effects of sulphur at lower temperatures than those used for forging. There is one case where sulphur commonly occurs. Nearly all carburizing compounds contain considerable sulphur, as evidenced by the strong odor of hydrogen sulphide when treated with acid. No effect has been

noticed either as to sulphur content or scaling action when carburizing as high as 1700 to 1750 degrees Fahr. Such an atmosphere would, of course, be strongly reducing and no checks have been made by the writer of actual sulphur content of gases.

On page 517 it is mentioned that the maximum penetration is 0.01 inch per hour. The rate for heating for forging is frequently stated as 20 minutes per inch but checking of actual rates shows 1-inch bars heated to forging temperature in 6 minutes and 4-inch bars in 35 minutes; therefore in regard to conclusions 6 and 7 the author's figures show that after removal of surface in the flash and cleaning by pickling or sandblast the effects of such an atmosphere would not be injurious in many cases. Any machining would be certain to eliminate the surface defects. It is quite possible, however, that flanges on axle I-beams, etc., and other thin sections would be sufficiently attacked to make starting points for fatigue failure. The scaling loss is, of course, a disadvantage in all cases.

Table III shows some unexpected results. Except in one case (which appears to be a typographical error) the scaling loss at 2300 degrees Fahr. is only about half that occurring at 2000 degrees Fahr. Table IV shows the same relation to a less marked extent. It would be interesting to know if the author has found this to be consistent in any other experiment he has conducted.

Author's Closure

The author appreciates the able discussions of this paper. Mr. McMullan has mentioned the fact that in some cases the high sulphur outer layers are probably entirely removed in subsequent operations with no injurious consequences to the forging. This is, of course, true and yet, as he points out, there are instances where subsequent operations may fail to remove this somewhat porous, weak outer case, and in this event considerable damage is possible.

Mr. McMullan also raises a question concerning the relative scaling losses at 2000 and 2300 degrees Fahr., as given in Tables III and IV. The answer to this seems to the author to lie in the rather crude methods of scale removal which were made necessary because of the information desired. The very crudity of these methods has, of course, introduced a considerable error in the determinations of loss in weight, particularly when the atmosphere used is nearly nonscaling to steel. Again it was somewhat easier to remove completely the scale at the lower temperature than at the higher. For these reasons it is believed that the difference in scaling actions at 2000 and 2300 Fahr. is only apparent and not actual. In the entire forging program lower temperatures have not been observed to yield greater amounts of scale with the same atmospheres.

The experience of the steel plant located near a sulphuric acid works related by Mr. Ashdown is an interesting case of sulphur absorption. It would be interesting indeed to know what values the sulphur gases attained in the atmosphere and to what extent the sulphur was absorbed in the steel. The question regarding the scaling losses at 2000 and 2300 degrees Fahr. shown in Tables III and IV has already been answered in the reply to Mr. McMullan.

FACTORS INFLUENCING THE ANNEALING OF COLD ROLLED STRIP STEEL

By G. R. Brophy and L. L. Wyman

Abstract

Two factors, normality and the degree of cold reduction, have been studied for their influence on the spheroidization of carbides in high carbon cold-rolled steel strip. It was found, in general, that with increasing amounts of cold work the steel became softer after annealing at any temperature up to the lower critical. Above this temperature the hardness obtained was increased and became more uniform for all reductions.

Up to the lower critical temperature, normal steels yielded lower hardness values than did the abnormal. But at their respective critical temperatures, which appear to be the best spheroidizing temperature, the abnormal steel yielded much better results. Also, it is shown that for the normal steel the minimum hardness, and the temperature at which this minimum is obtained, are dependent upon the amount of cold reduction, being lower for high reductions. On the other hand with abnormal steel, lower and consistent hardnesses were obtained at practically a constant temperature for all degrees of cold work. The temperature, however, was higher than for normal steel.

The experiments were followed metallographically and micrographs are presented to illustrate the structural changes. It appears from thermal analyses that the abnormal steel has a higher critical than the normal.

Introduction

In the annealing of cold-rolled strip steel it is desired not only to soften the metal, but also to retain the bright mirror-like condition of the rolled surface. Any oxidation coloring or graying of the surface is undesirable.

In the past, the customary practice has been to anneal this material by packing coils of strip in cast iron borings, and subject this

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The authors are members of the society and are associated with the Research Laboratories of the General Electric Co., Schenectady, N. Y. Manuscript received June 15, 1932.

mass to long-time anneals in gas- or oil-fired furnaces. While this method is capable of yielding quite satisfactory results, it is expensive, as well as slow and dirty.

Within the last few years, however, there has been developed an electric furnace of the bell type which uses a protective atmosphere, and eliminates the inconvenience and expense of packing material. The heating cycle is reduced, and the system becomes much more flexible, thus readily accommodating itself to changes in production demands.

In order to obtain consistently the best results with this equipment, because of the shorter annealing cycle, it is of greatest importance, especially when high carbon steel is annealed, that the raw material, and its processing, be carefully controlled, as the results of the following experiments will show.

The process of annealing high carbon cold-rolled steel should soften this material by causing the spheroidization of its carbide. This is usually accomplished by heating at, or just under, the A_1 temperature for an extended period of time; for example, in the electric furnace a six to eight hour treatment, at temperature, for a five-ton load.

Satisfactory results have usually been obtained, but frequent occurrences of wide variations in the hardness and ductility of the annealed steel, even in a single load, were quite disconcerting.

When it is taken into consideration that these atmosphered electric furnaces are so designed and built that the temperature within a loaded furnace at heat does not vary more than 15 degrees Fahr., the causes of these irregularities must be found elsewhere.

The spread of results under these conditions of furnace operation clearly indicates a variety of conditions in the nature of the material being used. These are: (1) a known and unavoidable variation in the degree of cold work in the steel strip; (2) possible composition differences; and (3) the possible influence of differences in degree of normality.

Relative to the first condition mentioned above, there is a definite but unavoidable variation caused by the economics of mill operation.

The common practice is to stock relatively few sizes of the hot-rolled wire (strip) bar, and to use this stock as raw material for a large number of sizes of cold-rolled strip. As a result of this, the mill run of material to be annealed covers a wide range of cold reductions, the effects of which have been studied in the following experiments.

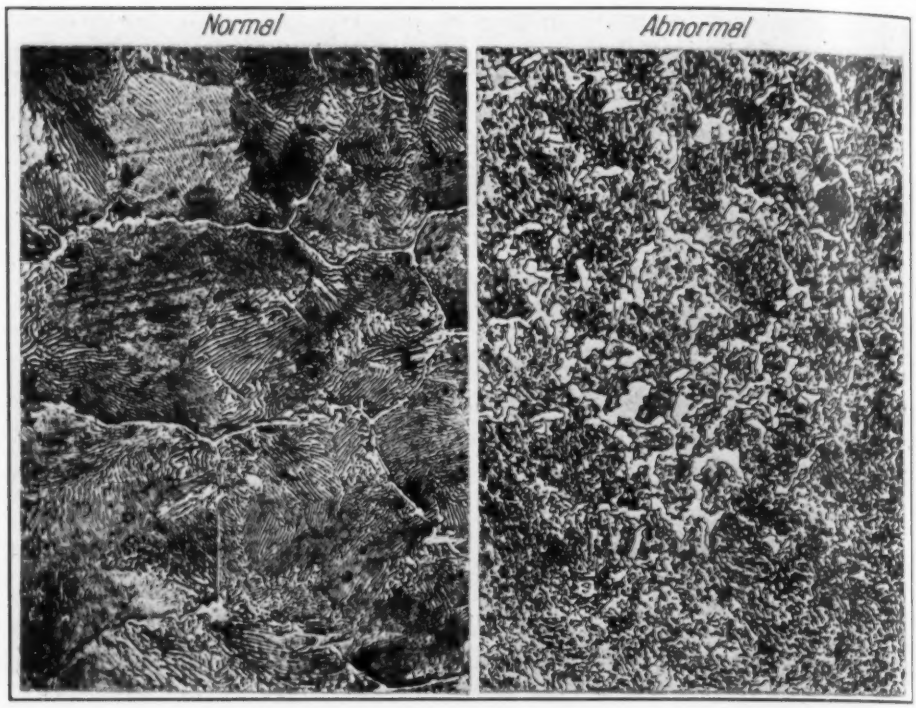


Fig. 1—Photomicrograph of Steel Having a Coarse-grained but Normal Structure with Well-developed Pearlite and Cementite Network.
Fig. 2—Photomicrograph of Steel Having An Extremely Abnormal Structure. These are the Steels Used in this Investigation.

The second variable undoubtedly exists, but for purposes of this investigation was eliminated by selection of material.

The third variable was really the unknown, but an excellent possibility in view of the difference in personality which steels have been shown to possess by Shepherd[1], Luerssen[2] and others.

Epstein and Rawdon[3] in their experiments found that a more complete spheroidization occurred in abnormal steel than in normal, when these were cooled slowly through the critical range, and Sauveur[4], in discussing Grossmann's work on oxygen in steel, sug-

[1]B. F. Shepherd, "Inherent Hardenability Characteristics of Tool Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 17, 1930, p. 90.

[2]G. V. Luerssen, "Some Notes on the Behavior of Carbon Tool Steel on Quenching," TRANSACTIONS, American Society for Steel Treating, Vol. 17, 1930, p. 161.

[3]S. Epstein and H. S. Rawdon, "Progress in Study of Normal and Abnormal Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 337.

[4]Marcus A. Grossmann, "On Oxygen Dissolved in Steel, and Its Influence on the Structure," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 41.

gested that a steel rich in oxygen (abnormal) would spheroidize more readily than one poorer in that element.

Material

Samples of fifteen coils of hot-rolled strip 1.75 x 0.081 inches were furnished by the Thompson Wire Company, Matapan, Mass., the balance of the coils being marked and held for our disposition.

These samples were tested for normality by being packed in carburizing compound and heated at 930 degrees Cent. (1705 degrees Fahr.) for six hours and cooled slowly in the furnace. They were then examined microscopically and the two extreme samples selected as being suitable for further experiment. One, the structure of which is shown in Fig. 1, was coarse-grained normal; and the other, Fig. 2, was extremely abnormal, with well-developed pearlite and cementite network.

The analyses of the two steels are as follows:

	Abnormal Per Cent	Normal Per Cent
Carbon	0.73	0.71
Manganese	0.45	0.46
Silicon	0.07	0.07
Chromium	0.05	trace
Nickel	none	none
Vanadium	none	none
Aluminum Oxide	none	none

The other samples, while not being used for further experiment, were interesting in that they showed various degrees of normality and, in some instances, decidedly abnormal structures were found on the surfaces, while normal structures were found in the center. Segregations of normality and abnormality have been reported in rimming steel by Epstein and Rawdon, but they found the surface to be normal.

Experimental

A sufficient amount of each strip in the hot-rolled condition was rolled cold so that samples were obtained having reductions from 10 to 80 per cent. This rolling was done without annealing. It was noticed that as the reductions approached 30 to 40 per cent the materials hardened to a large extent, and reductions in this range were difficult, but further reductions became easier. The normal steel with about 60 per cent reduction began to show edge cracks. The ab-

normal steel rolled much easier on the whole, and did not develop edge cracks at any stage of reduction used.

Samples of all reductions were annealed collectively at each temperature used from 600 to 800 degrees Cent. (1110-1470 degrees

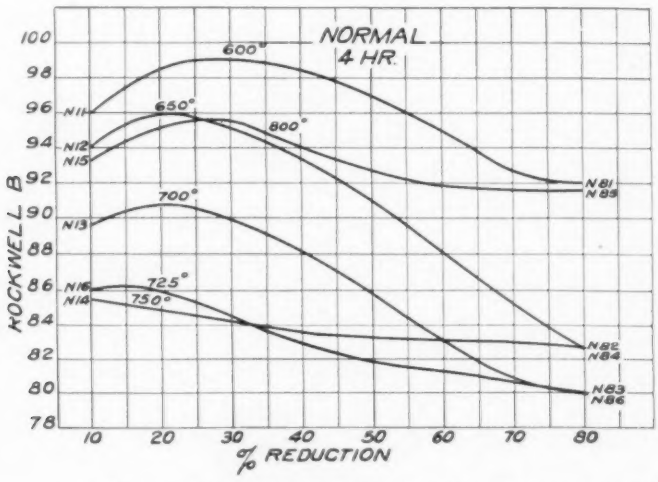


Fig. 3—Rockwell Hardness Results Plotted Against Per Cent Cold Reduction—Normal Steel.

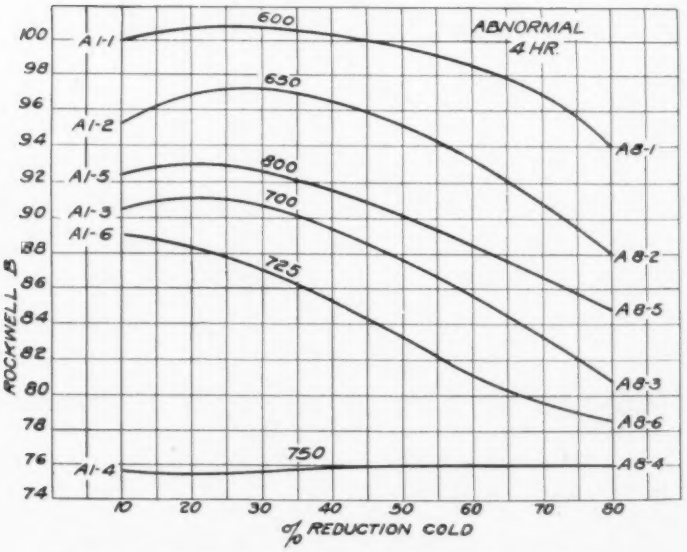


Fig. 4—Rockwell Hardness Results Plotted Against Per Cent Cold Reduction—Abnormal Steel.

Fahr.). The samples were packed in spent carburizing compound to prevent scaling and decarburizing and heated for four hours at temperature, then cooled in the furnace. The annealed pieces were then tested for Rockwell hardness using the standard B scale.

Fig. 3 shows the results plotted against per cent cold reduction for the normal steel. In all cases there is a general reduction of hardness with increasing cold reduction for any given temperature. Up

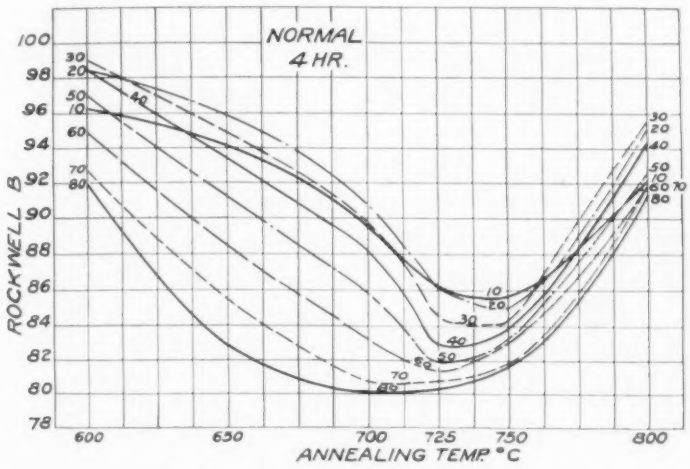


Fig. 5—Rockwell Hardness Results Plotted Against Annealing Temperatures for Various Reductions—Normal Steel.

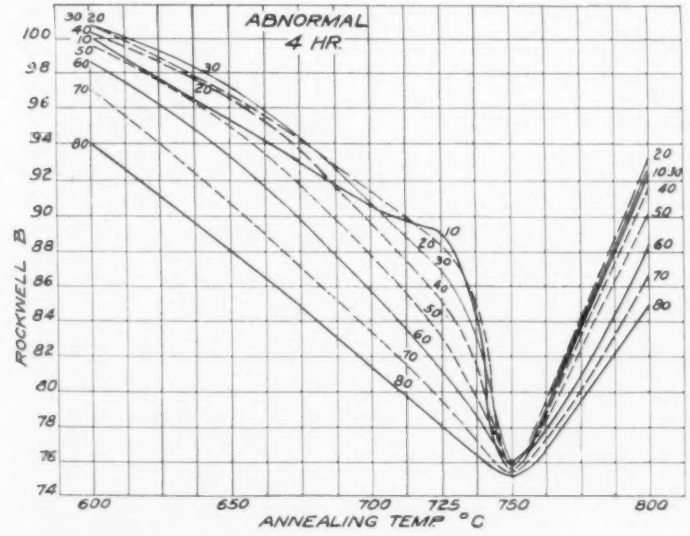


Fig. 6—Rockwell Hardness Results Plotted Against Annealing Temperatures for Various Reductions—Abnormal Steel.

to about 30 per cent, however, there is an increase which becomes less marked as the annealing temperature increases. The minimum hardness of Rockwell B 80 is obtained by annealing at 725 degrees Cent. (1340 degrees Fahr.).

Fig. 4 shows the results for the abnormal steel. Again the hardness decreases, in general, for increased reductions above 30 per cent. In this instance, the minimum hardness occurs when the steel is annealed at 750 degrees Cent. (1380 degrees Fahr.). The hardness is lower than was obtained with normal steel and quite uniform for all reductions, thus differing materially from the normal steel. It is to be noted, however, that annealing below this temperature gave lower values for the normal than for the abnormal steel.

In both cases annealing at temperatures higher than the critical point results in increased hardness caused by the re-solution of carbides, and the formation of, or tendency to form, of pearlite on slow cooling. In this case, brittleness is quite marked, especially in the normal steel.

Figs. 5 and 6 show the same data replotted against annealing temperatures for various reductions. These curves are very illuminating and will merit careful consideration.

It will be seen, in the case of the normal steel Fig. 5, that the minimum hardness values are obtained at successively lower temperatures as the amount of cold reduction increases. The temperature range of these minima is from 700 to 730 degrees Cent. (1290-1345 degrees Fahr.) for the reductions used.

The minimum hardness obtained with the abnormal steel seems to be independent of the degree of cold work provided the annealing temperature is correct, namely 750 degrees Cent. (1380 degrees Fahr.). This point has real and practical significance.

The difference in the temperature at which maximum softening occurs suggests a difference in the temperature at which the A_1 point occurs in these two types of steel.

Thermal analyses of the two steels confirm this, for on heating A_1 was found to occur at 745 degrees Cent. (1370 degrees Fahr.) for the abnormal and at 730 degrees Cent. (1345 degrees Fahr.) for the normal, but upon cooling the A_1 for the abnormal is but five degrees higher than that of the normal. As has been described by Epstein and Rawdon, the difference in the reactions was decided, the abnormal steel showing a sharp intense point while the normal steel shows a more sluggish reaction.

Microscopic Examination

The degree and completeness of an anneal on this material can

be judged by (1) the amount of distorted structure, as indicating the residual effects of the cold work, and (2) the degree of spheroidization of the carbide in the steel.

In considering the results of the heat treatment, it will be noted that in the series of photomicrographs all of the heaviest reductions show the effects of cold work, up to the 700 degrees Cent. (1290 degrees Fahr.) anneal.

For the purpose of more clearly depicting the changes due to the different degrees of cold work, it was deemed advisable to show not only the maximum and minimum reductions, but also to include an intermediate degree of cold reduction. To serve this end, the series of photomicrographs of 40 per cent reduction is included. This 40 per cent series is not to be interpreted as representing a definite change point, but is merely intended as an indicator of the gradual changes which have taken place up to that point.

At this temperature of 700 degrees Cent. (1290 degrees Fahr.) the abnormal steel retains the cold work effect, but the ferrite of the normal steel for higher reductions has regranulated; that is, the cold work strains have been relieved. This annealing effect is quite definite on both the 40 per cent and 80 per cent reductions.

When the annealing temperature is at 725 degrees Cent. (1335 degrees Fahr.) it is noted that the normal steel in the lower reductions has regranulated, but the abnormal steel still shows the effect of the cold work.

The annealing of these steels at 750 degrees Cent. (1380 degrees Fahr.) has regranulated both of them, and there are no evidences of residual cold work.

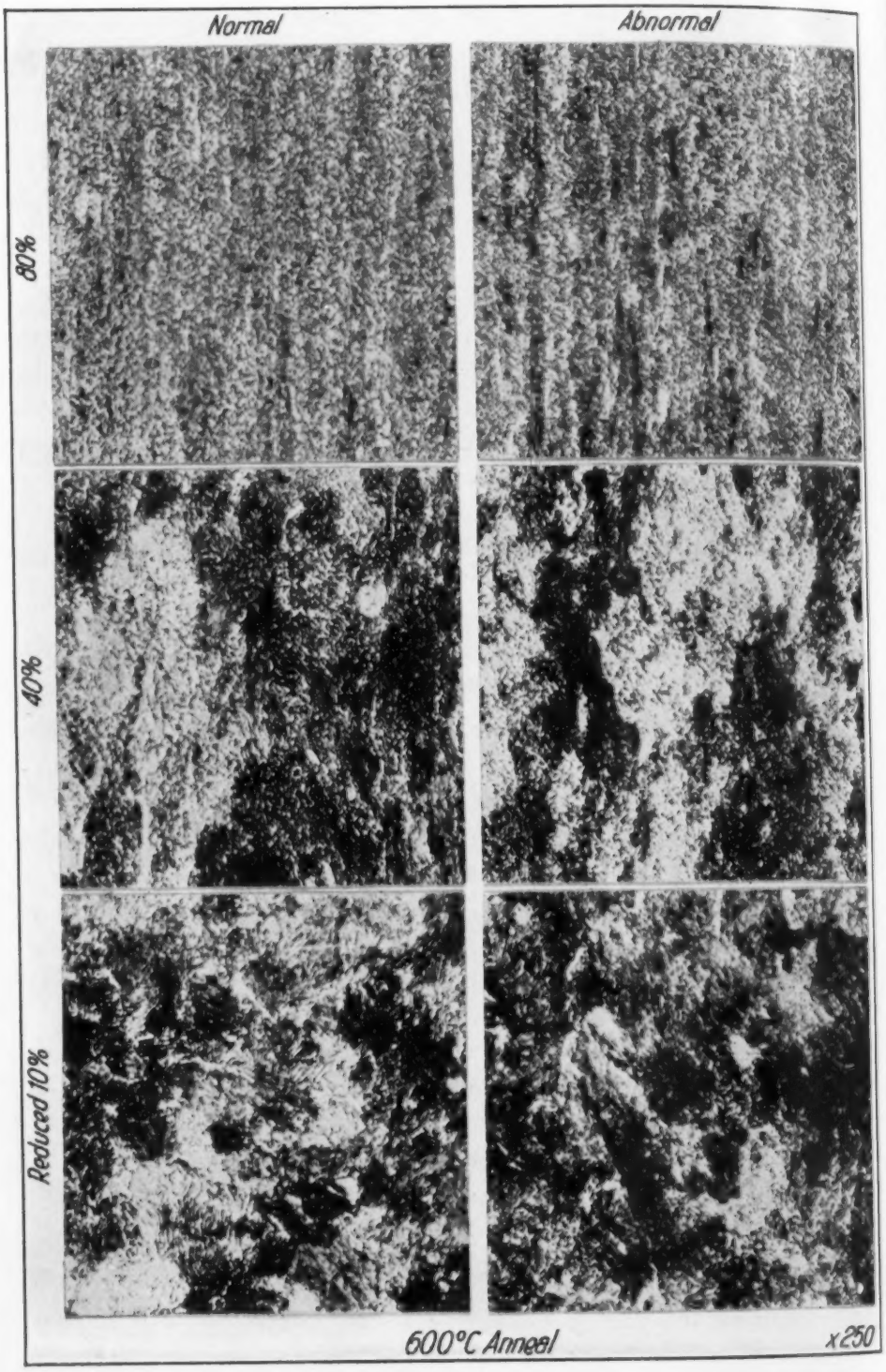
The abnormal steel shows slight indications of pearlitic structure in the lowest reductions, but none in the heavier reductions.

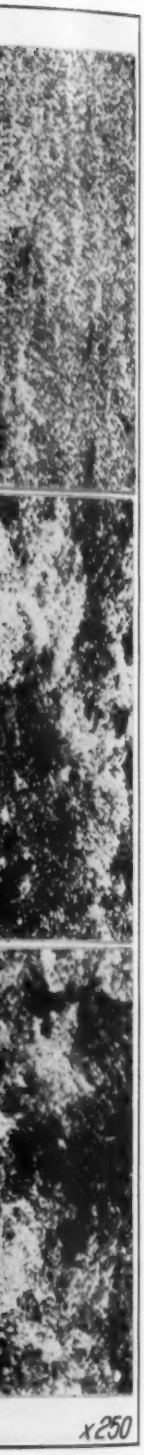
The normal steel, however, shows some pearlite in the 80 per cent reduction and increasing amounts of pearlite with decreasing reductions.

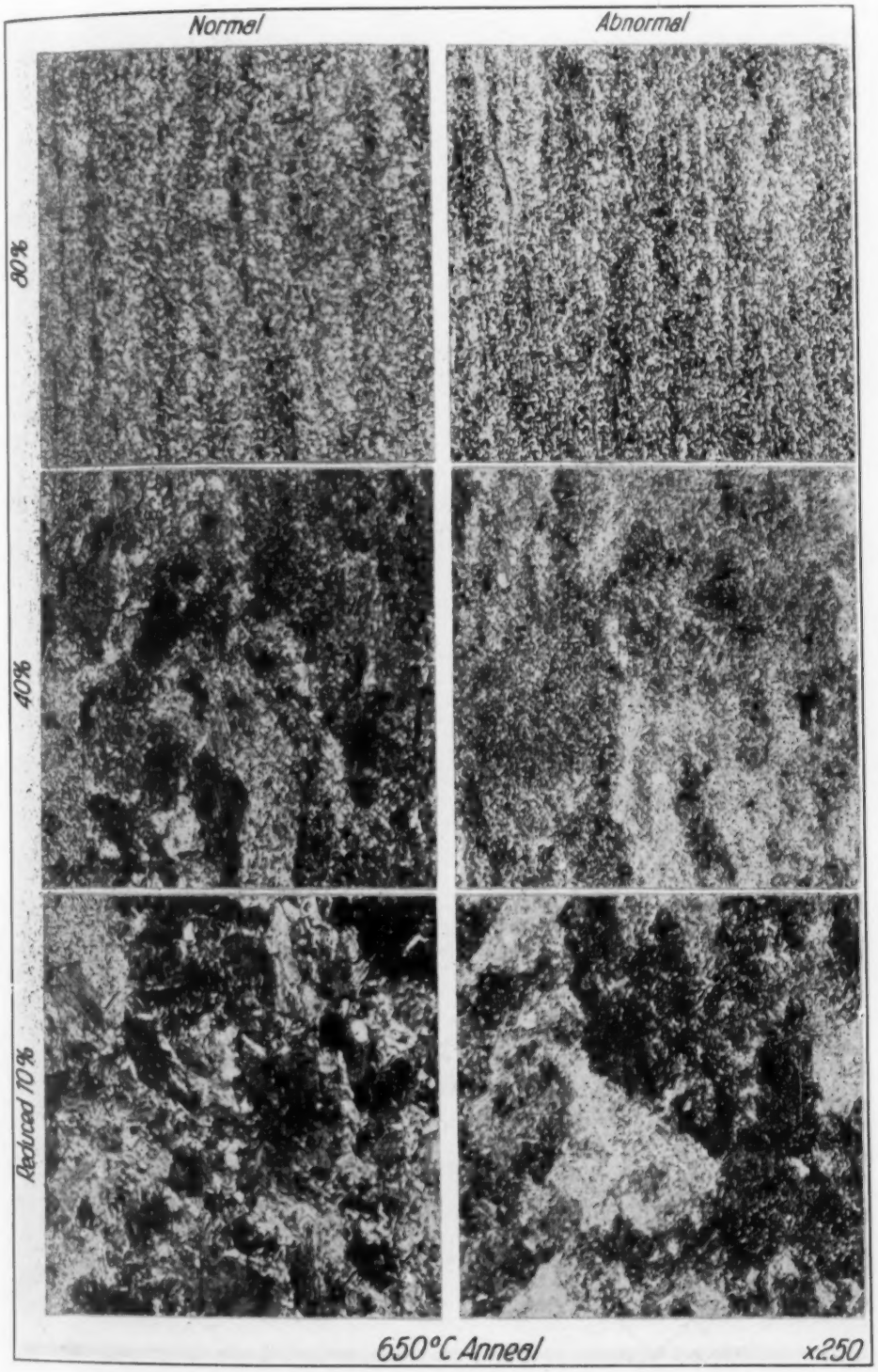
After treatment at 800 degrees Cent. (1470 degrees Fahr.) both of these steels appear to be predominantly pearlitic.

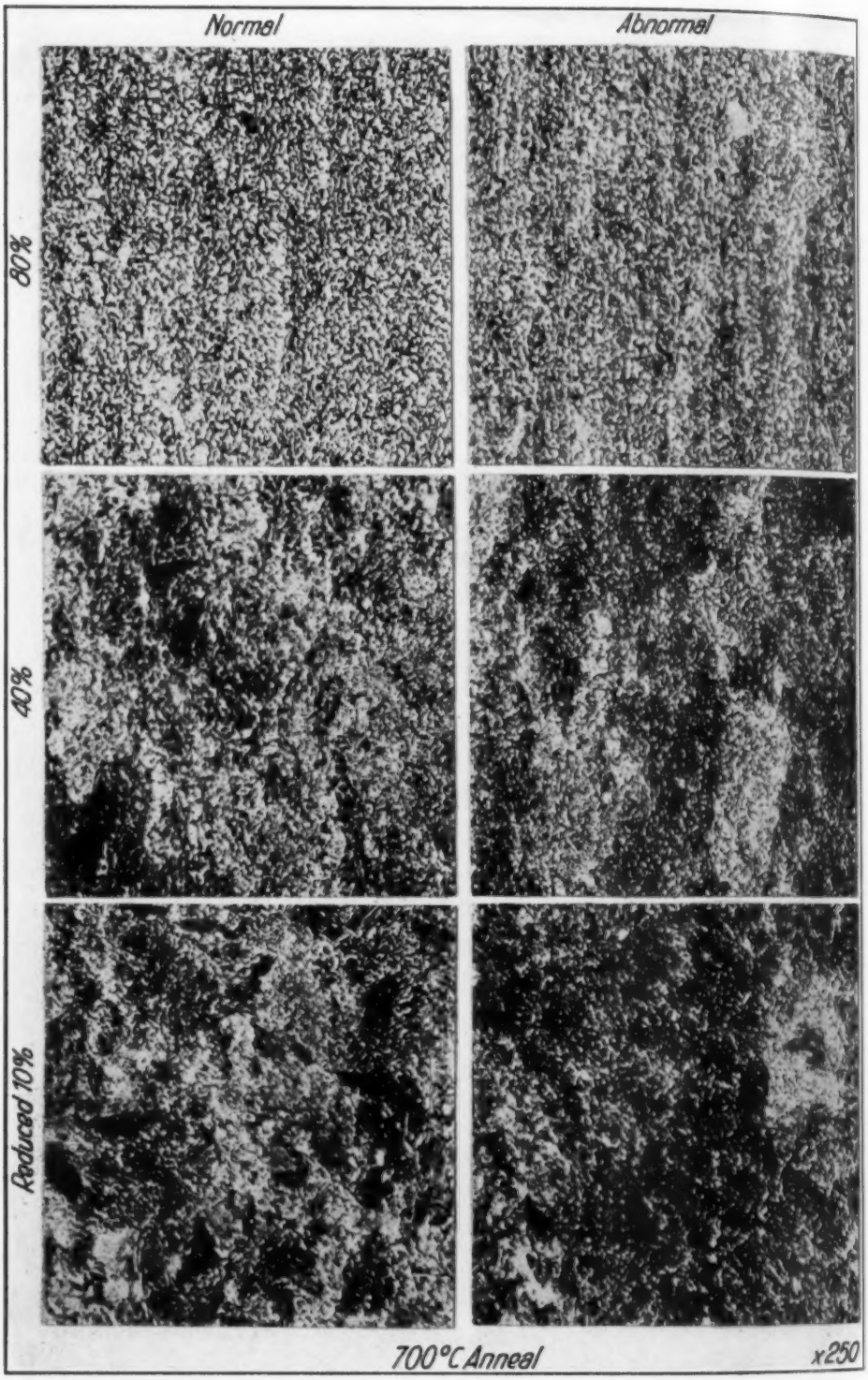
In order to further elucidate the actual changes transpiring during this series of heat treatments, the samples were examined at higher magnification—the second series of photomicrographs showing the changes that take place.

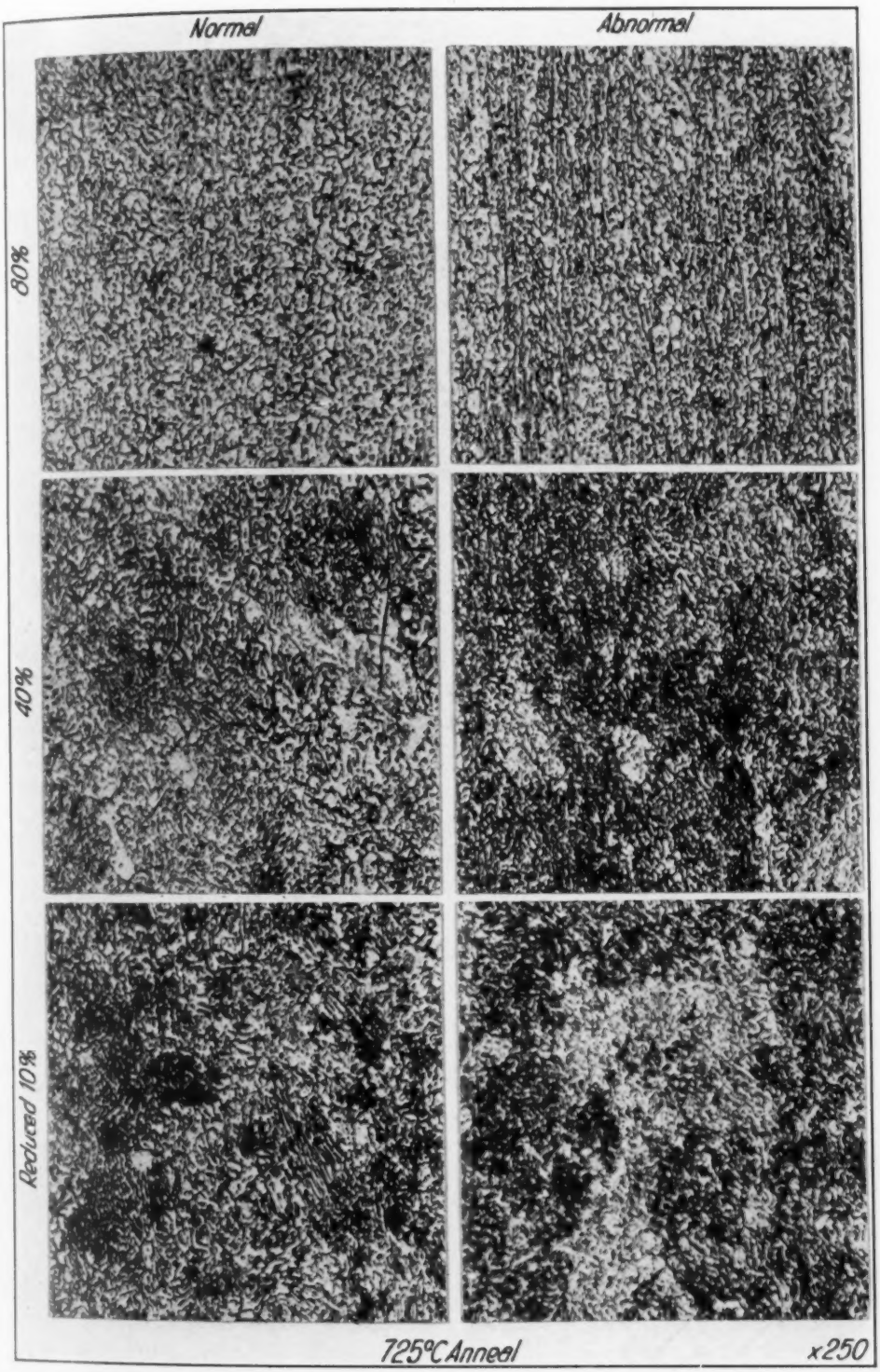
The examination of this series shows that the abnormal steel, which already shows practically complete spheroidization even at the

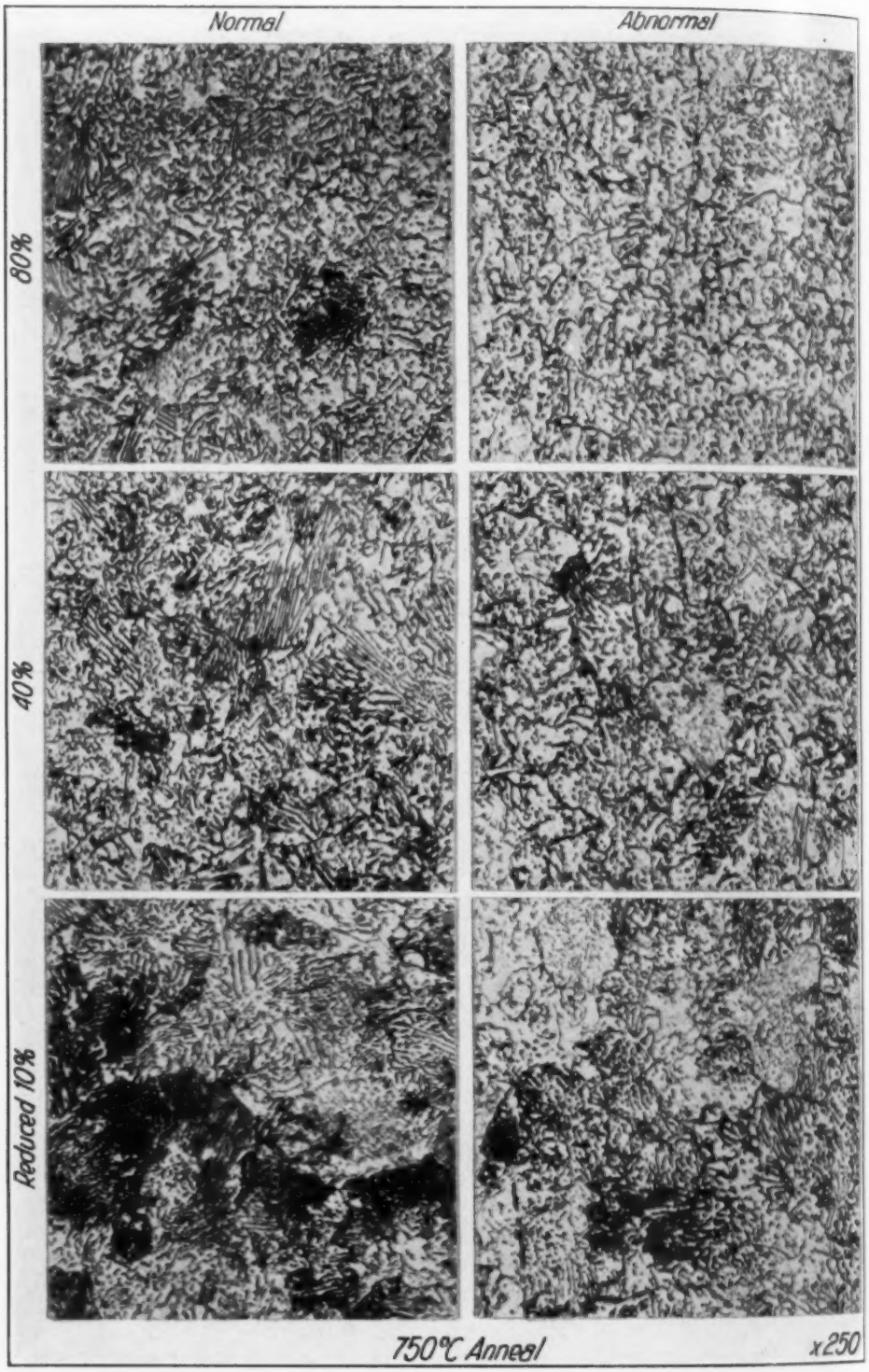

Normal
Abnormal
80%
40%
Reduced 10%
600°C Anneal
x250

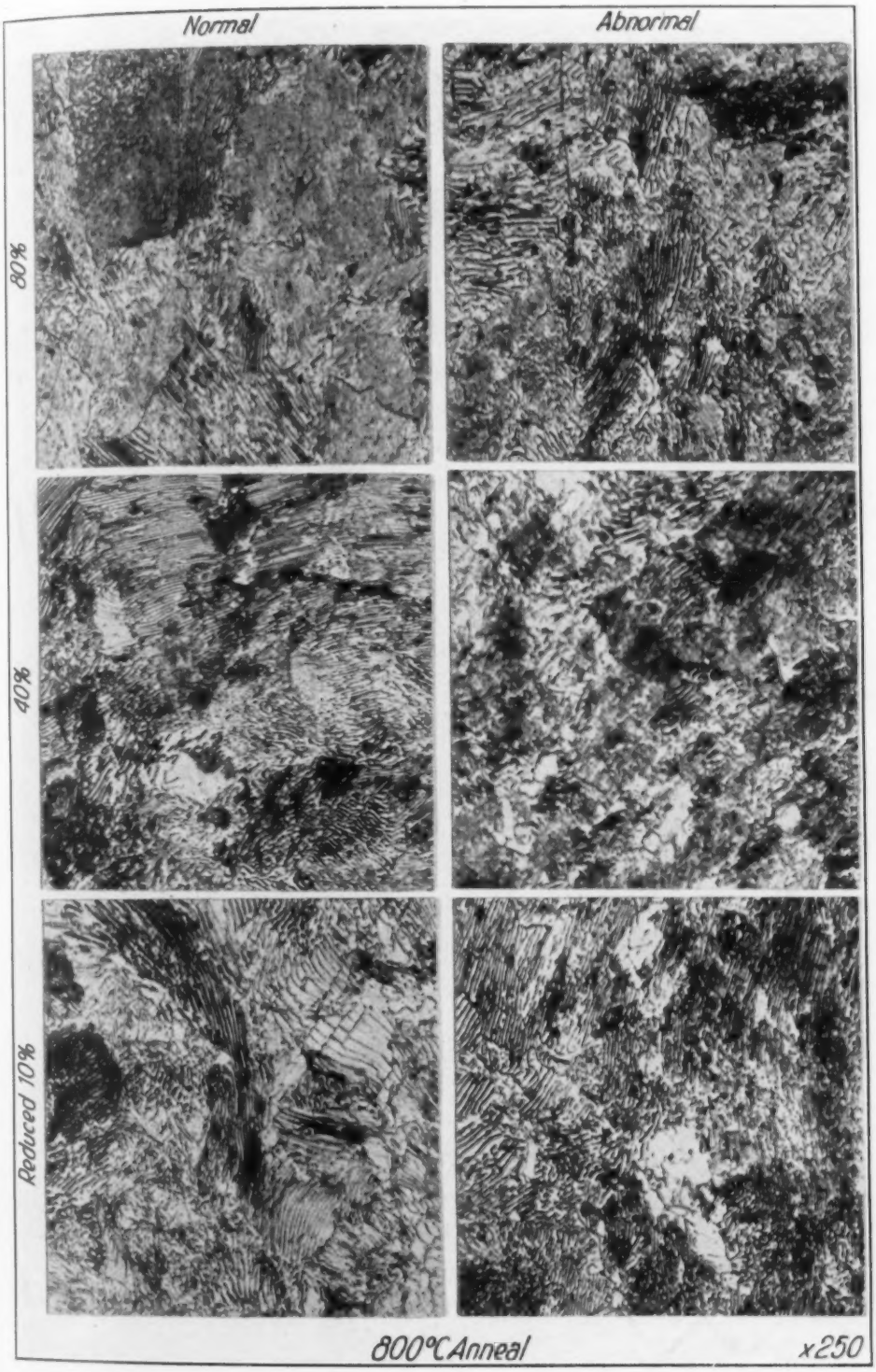

x250

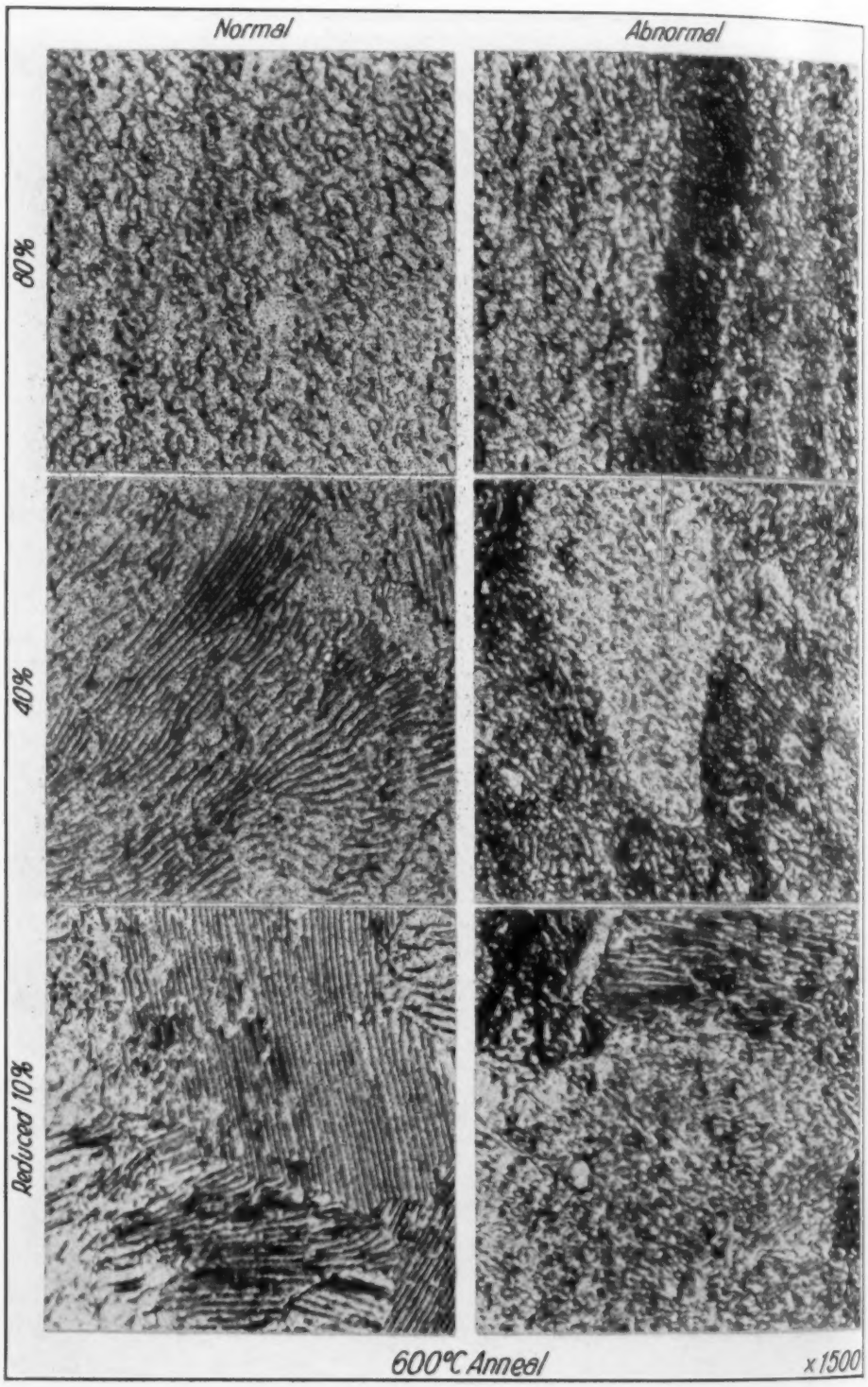

Normal
Abnormal
80%
40%
Reduced 10%
650°C Anneal
x250

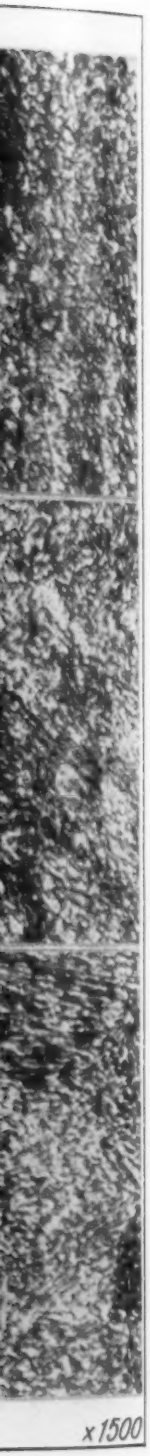

Normal
Abnormal
80%
40%
Reduced 10%
700°C Anneal
x250

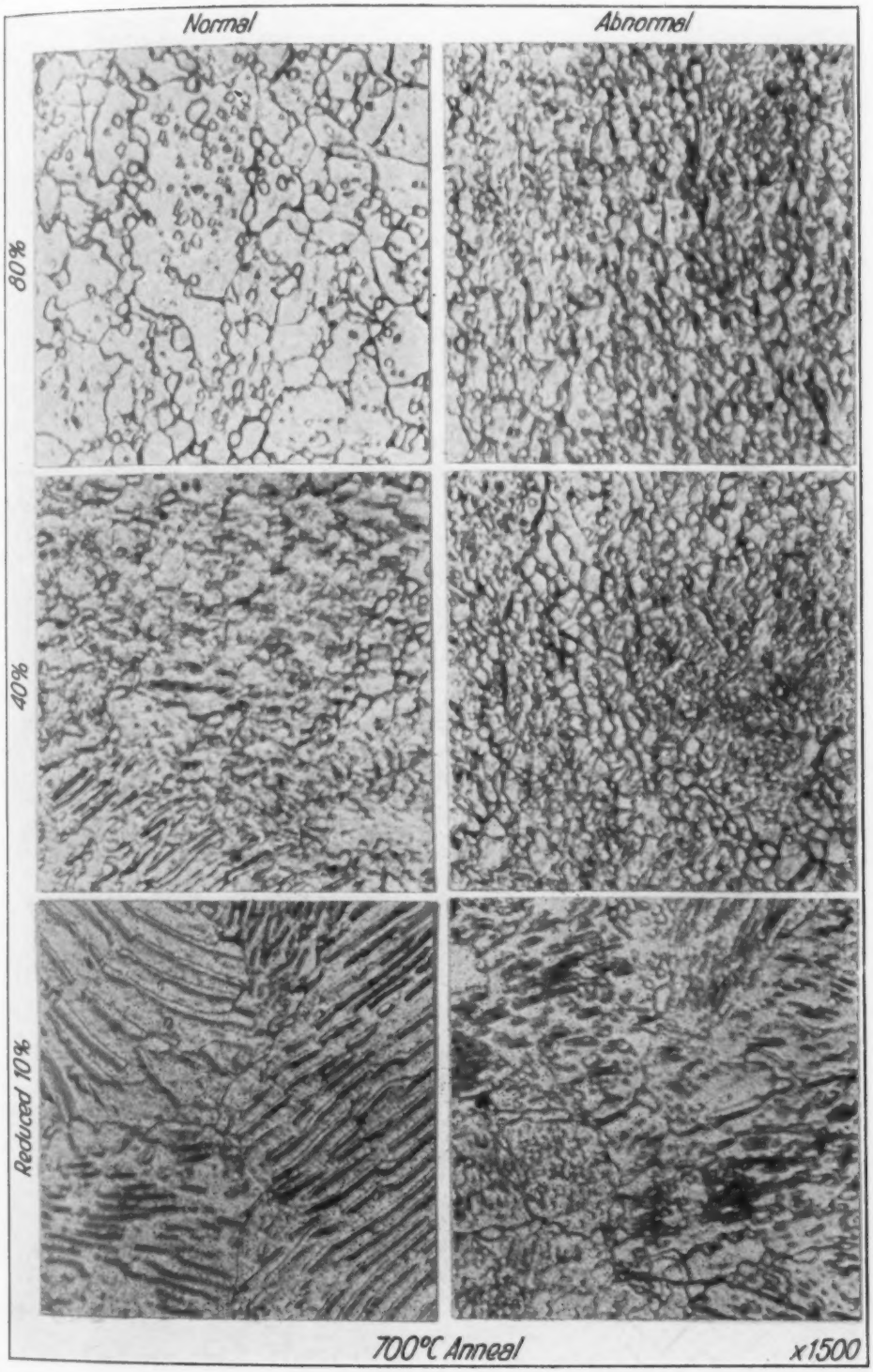

Normal
Abnormal
80%
40%
Reduced 10%
725°C Anneal
×250

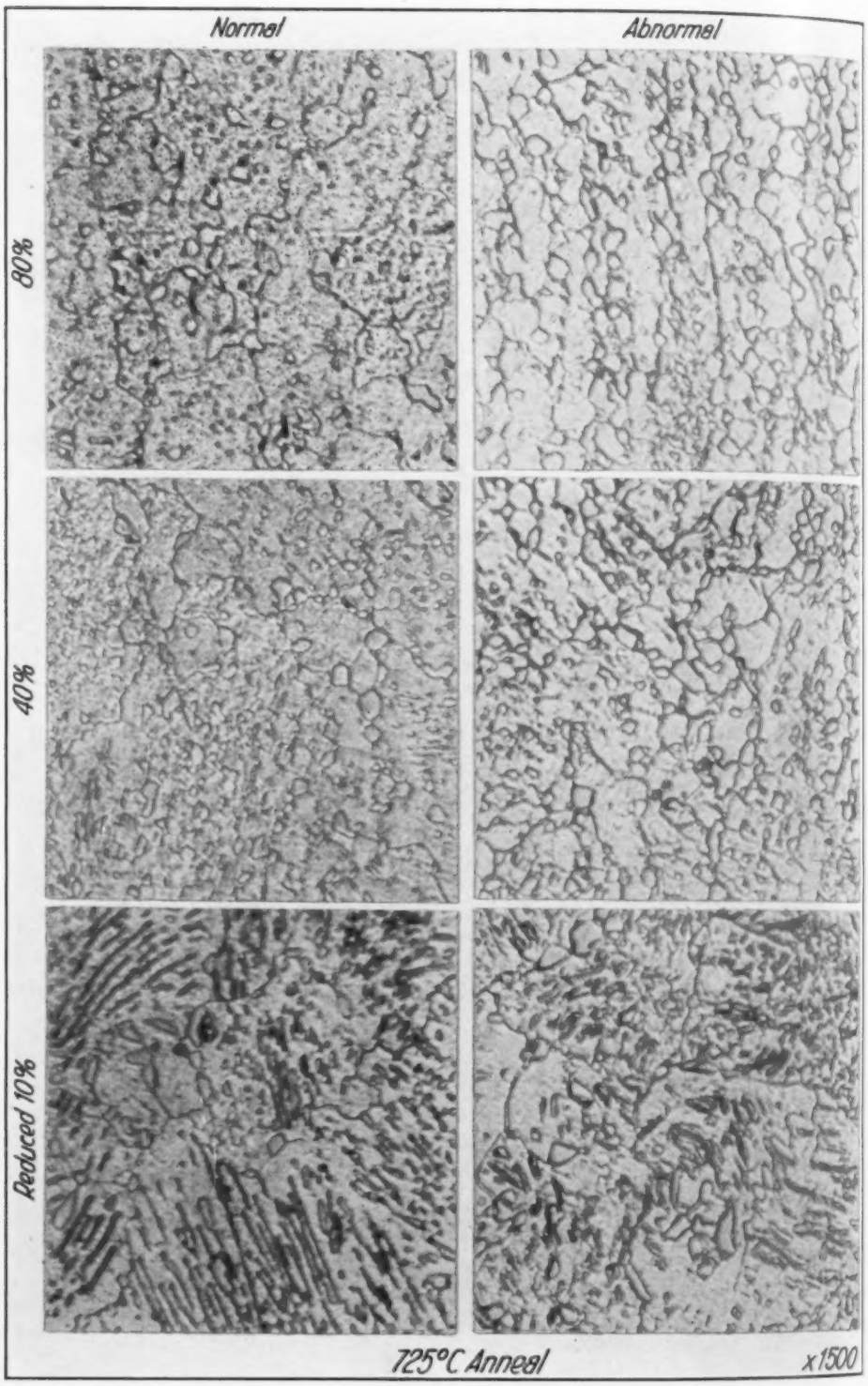

Normal
Abnormal
80%
40%
Reduced 10%
750°C Anneal
x250

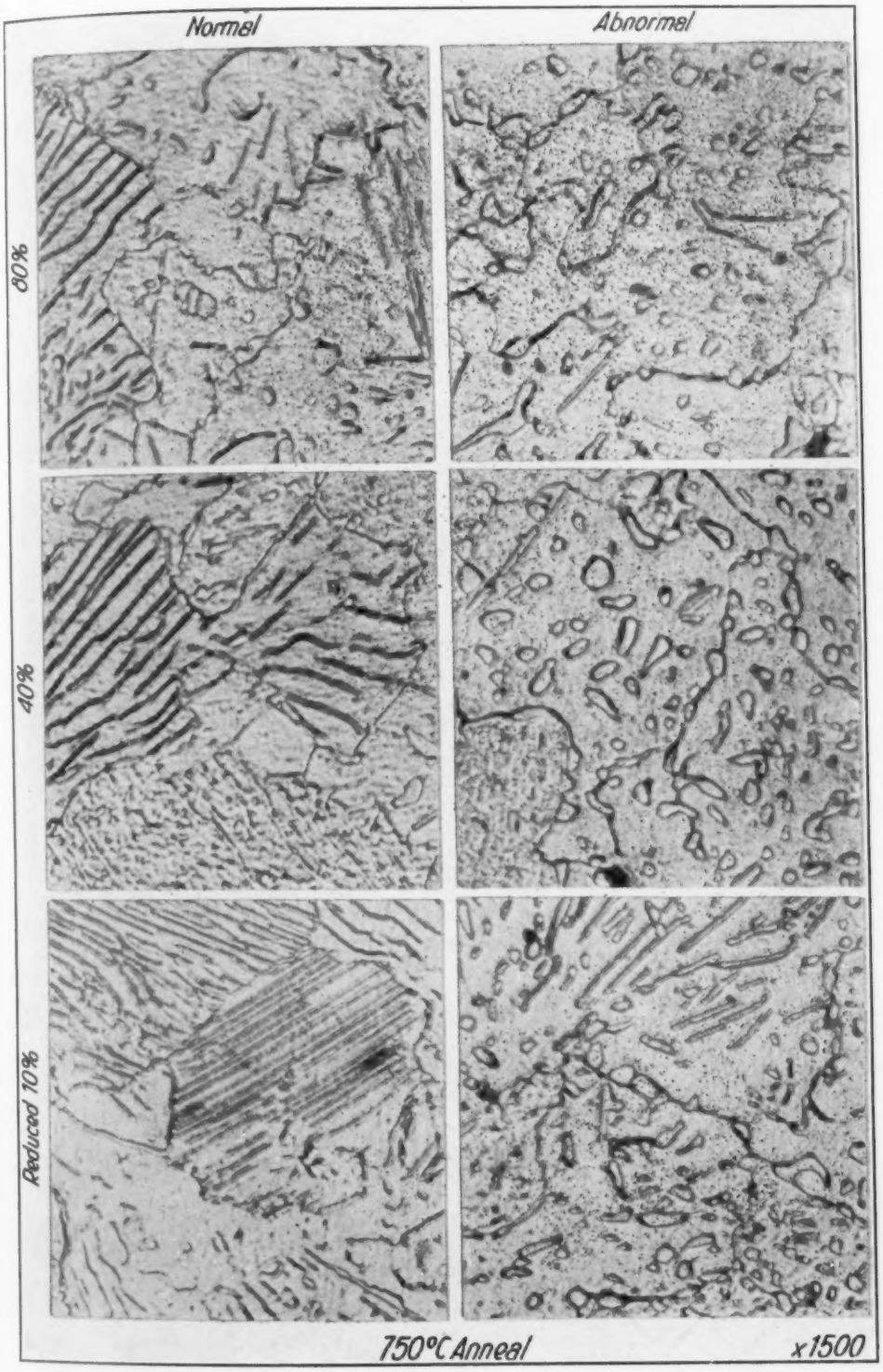

Normal
Abnormal
80%
40%
Reduced 10%
800°C Anneal
x250

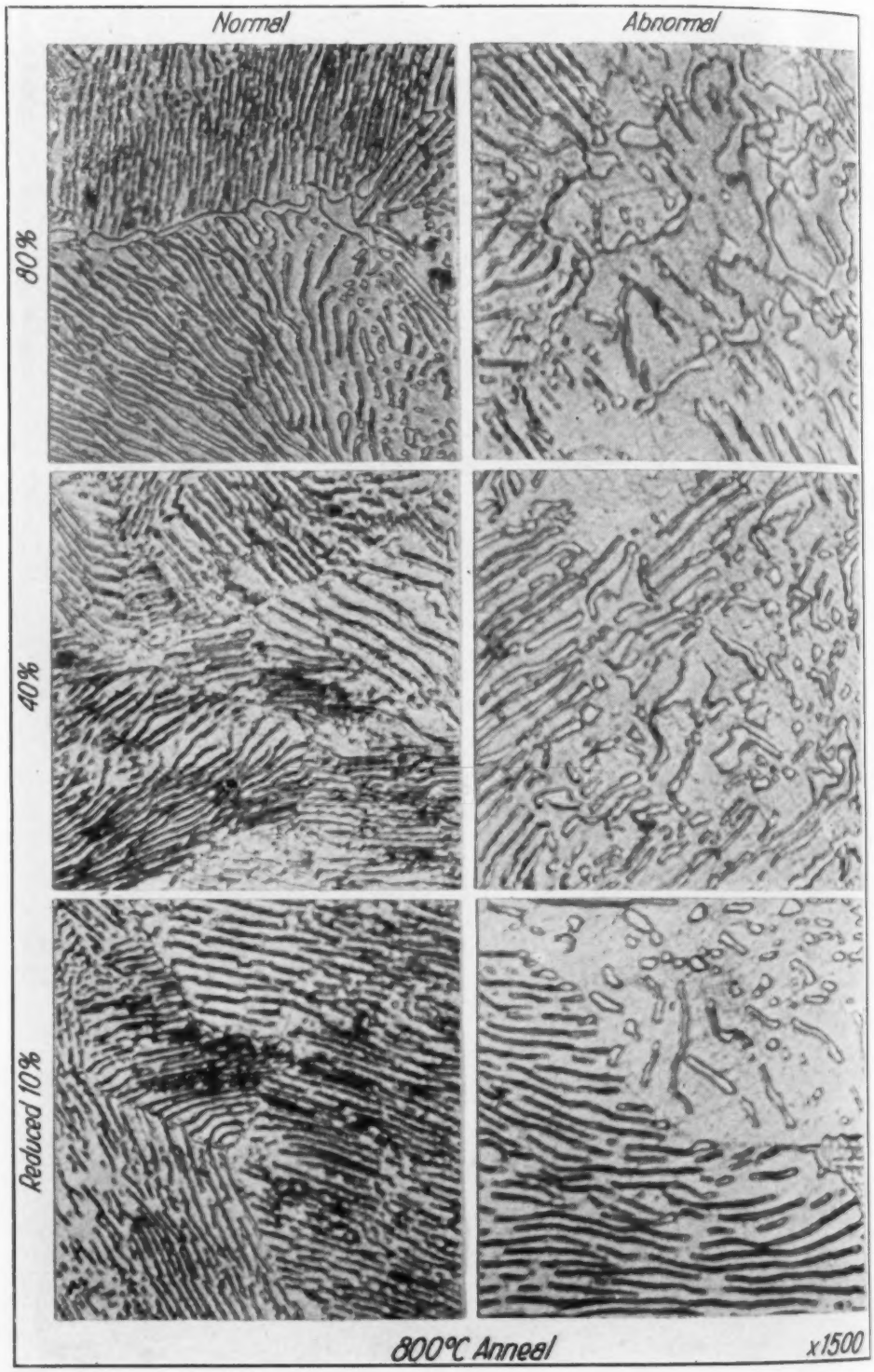

Normal
Abnormal
80%
40%
Reduced 10%
600°C Anneal
x1500


x1500


Normal
Abnormal
80%
40%
Reduced 10%
700°C Anneal
x1500


Normal
Abnormal
80%
40%
Reduced 10%
725°C Anneal
x1500


Normal
Abnormal
80%
40%
Reduced 10%
750°C Anneal
x1500


Normal
Abnormal
80%
40%
Reduced 10%
800°C Anneal
x1500

lowest annealing temperature, does not change materially as the temperature increases to 750 degrees Cent. (1380 degrees Fahr.). The structure becomes somewhat coarsened with increasing temperature, but the cold work effects still persist in the higher reductions, and the pearlitic indications still remain in the lowest reduction.

The results in evidence on the normal steel, over this same range, are quite different. After the 600 degrees Cent. (1110 degrees Fahr.) treatment, the normal steel is decidedly pearlitic, except in the heaviest reductions.

As the temperature is increased to 700 degrees Cent. (1290 degrees Fahr.), the lowest reductions are still decidedly pearlitic, but now the 40 per cent shows but traces of residual pearlite. Increasing the temperature to 725 degrees Cent. (1335 degrees Fahr.), it is noted that only the lowest reduction shows even the slightest indication of a pearlitic nature.

Inasmuch as 725 degrees Cent. (1335 degrees Fahr.) is slightly below the critical point for this material, it is only fair to conclude that a heat treatment at the critical point would produce a complete regranulation and spheroidization in this steel, regardless of the degree of cold work.

The normal steel has then shown that, as the temperature of the treatment increases, the regranulation and spheroidization affects successively lower reductions.

When the temperature of the heat treatment has reached 800 degrees Cent. (1470 degrees Fahr.), the normal steel is very definitely composed of fine lamellar pearlite.

The abnormal steel shows fine pearlite in the lower reductions, but as the amount of reduction increases, the pearlite decreases and the massive carbide increases, such structures being quite characteristic of this material.

Interpretation

The results of the hardness determinations brought out a very striking difference in the reactions of these steels to the same heat treatments.

The photomicrographs show that, regardless of the degree of cold work, the abnormal steel gave minimum hardness readings at 750 degrees Cent. (1380 degrees Fahr.), just slightly above its A_1, whereas the normal steel gave minimum hardness readings at successively lower temperatures as the degree of cold work increased.

This latter can but be interpreted to mean that at any temperature below about 700 degrees Cent. (1290 degrees Fahr.), the degree of cold work is the controlling factor in the annealing of the normal steel, so that the annealing temperature is definitely a function of the degree of cold work.

As may be seen in the photomicrographs, there are two processes simultaneously taking place in this normal steel. The first is the increased regranulation with increasing temperature, and the second is the increased spheroidization with increasing temperature. Considering that both of these factors influence the hardness in the same direction, it is quite evident that the slope of the hardness curves should be quite gradual and not show a marked "break" to the minimum hardness.

The results of the microscopic examination substantiate this inasmuch as it was noted that as the temperature of the anneal was increased the lower reductions were increasingly affected.

This condition of constant shifting of the regranulation and spheroidizing actions culminates at the critical point for this steel, where the last traces of pearlite are eliminated.

In considering the abnormal steel, it is to be noted that the material is practically spheroidized at the lowest heat treatment given, 600 degrees Cent. (1110 degrees Fahr.), and that increasing the temperature of the heat treatment really does little other than coarsen the structure. Essentially the same amounts of residual pearlite persist in the lower reductions, and the cold work effects persist throughout the higher reductions.

However, when this material is annealed at 750 degrees Cent. (1380 degrees Fahr.), just above its A_1, there occur two major changes. First, all evidences of cold work have disappeared, and second, the ferrite has achieved an immeasurably greater grain size than can be attributed to a 25 degree Cent. increase in temperature, this being shown for all reductions.

Thus it is to be expected that at its critical point, the abnormal steel, regardless of the amount of cold reduction, should show a marked and abrupt decrease in hardness. These observations are in complete agreement with the hardness results which show a sharp decrease in hardness readings at the critical point.

The hardness curves on these two steels also show that for any reduction, and for any heat treatment below the critical points of these steels, the normal steel is the softer.

The answer is plainly evident in the photomicrographs, which clearly show that the normal steel is losing more and more of its cold work effect as the temperature increases, whereas the abnormal steel does not, and thus remains harder.

It is further evident that after annealing at and above the A_1, the abnormal steel is the softer. The reason for this appears to be due to its less pearlitic structure and large grain size.

Hardening

It is frequently mentioned that hardened abnormal steel is prone to soft spots. This has been attributed by Epstein and Rawdon to a higher critical cooling rate which would become of greater importance with larger sections. But with the rate of cooling obtained upon water quenching such thin sections as were dealt with in these experiments, no difference was expected between normal and abnormal steel.

Samples of each were hardened by water quenching from 775 degrees Cent. (1425 degrees Fahr.) and carefully explored for hardness. The Rockwell hardness ran uniformly C 62-63.

The normal steel fractured in a much more brittle manner than the abnormal steel, and showed a much coarser grain; the abnormal steel being quite resilient and possessing a fine, silky, grain structure.

Conclusions

(1) Annealing these two types of steel at any temperature below their respective critical ranges results in lower hardness values for the normal steel, for like reductions.

(2) For both steels, in general the hardness values after annealing decrease, with increasing cold reduction.

(3) The minimum hardness values for these steels are obtained when they are annealed at approximately their respective criticals, but it was found that for the normal steel, the minimum values occurred at decreasingly lower annealing temperatures as the cold reduction increased, the hardness also decreasing with increasing cold work. The abnormal steel, on the other hand, gives uniform minimum values at a constant temperature regardless of the amount of cold reduction. These minimum values for the abnormal steel are lower than the minimum values for the normal.

(4) Annealing above the critical increases the hardness values of each type of steel.

(5) Hardening these two types of steel from 775 degrees Cent. (1425 degrees Fahr.) gives much more satisfactory results in the abnormal steel.

(6) The results of these experiments demonstrate the practical advantage of using an abnormal type of steel.

DISCUSSION

Written Discussion: By H. S. Rawdon, chief, division of metallurgy, U. S. Bureau of Standards, Washington, D. C.

The authors are to be congratulated on this well planned and well executed investigation which in the writer's opinion is an exceedingly valuable contribution to the literature on the subject of abnormality in steel. The work is especially useful in a practical way since the practical aspects of the problem have been kept foremost throughout. Too often the term "abnormal," as applied to steel, a term which everyone recognizes as ill chosen but necessary for want of a better one, is considered as connoting an inferior or secondary material. It is a source of gratification, at least to the writer, that one of the important facts established as a result of this work is that the practical advantage of using an abnormal steel for the particular purpose in hand was unmistakably demonstrated by the investigation.

The authors state that for the purpose of this investigation the variable of composition which undoubtedly exists in commercial work, was eliminated by the selection of the material. The writer cannot concur with the implied conclusion that the presence of chromium to the extent of 0.05 per cent in one of the steels, the abnormal one, is of no significance. The influence of small amounts of chromium in retarding graphitization in high carbon tool steels is quite generally recognized and it is believed that the effect of this amount of chromium on the abnormal tendency of the steel used in this work is not entirely negligible.

The question may perhaps be in order as to the use of the Rockwell method for determining the hardness of the very thin sheets produced by cold rolling the hot-rolled material. An 80 per cent reduction on the hot-rolled sheet 0.081 inch in thickness resulted in strip only 0.015 inch thick. The hardness of such a thin sheet material, especially in the soft condition after annealing, probably would not be correctly given by the Rockwell method. The Vickers method would perhaps have been a wiser choice for this. Any possible change in the hardness curves, of course, would not detract in any way from the validity of the conclusions drawn by the authors. The point is mentioned only by way of precaution, in case the hardness figures are quoted as being the true hardness of steels of the composition given.

Written Discussion: By Samuel Epstein, Battelle Memorial Institute, Columbus, Ohio.

The authors, in pointing out the advantages of an abnormal type of steel

for cold-rolled strip, have added another example to those recently described by Shepherd and Luerssen among others, in which that aspect of "body" in steel known as abnormality may be of very practical benefit. Dealing as they have with the effects of reductions by cold working, the question of aging and embrittlement by cold work naturally arises. The "non-aging" structural steel Izett discussed by Neuendorf[1] is very fine-grained and abnormal. Samples of this material have been found to harden less after equal amounts of cold work than ordinary structural steel and also to be much more immune to embrittlement as measured by notched bar impact tests after cold work (up to 17 per cent reduction) and reheating to the blue heat region, than ordinary structural steel.

It is of interest to note, therefore, that the abnormal strip steel tested by the authors did not appear to become as hard (unfortunately the hardness values after cold working but before annealing are not shown in the paper) and brittle with cold work as the normal steel, for they state, "The normal steel with about 60 per cent reduction began to show edge cracks. The abnormal steel rolled much easier on the whole and did not develop edge cracks at any stage of reduction used." As a rule an abnormal steel will have a higher impact resistance than a similar normal steel. Not all abnormal steel has the unusual "non-aging" property of Izett, however. Although this property and abnormality apparently do not necessarily go together, they are probably related in some ways.

Both probably lie at the bottom of most of the mystery surrounding the term "body" in steel and similar synonymous terms which have lately arisen. The better appreciation and understanding of abnormality and aging which we are rapidly acquiring should remove much of that mystery, and replace such terms as "body" by more scientific concepts.

JOHN R. DAESEN:[2] I would like to ask if there was any difference in the ability to stand forming operations between the abnormal and the normal steels after they had been annealed. The fact that there was complete spheroidization long before the effects of cold work were removed is what raises the question in my mind. Is it a fact that the spheroidization is all that is necessary in order to get the best forming properties, or is it necessary to hit that sharply defined critical point in the case of the abnormal steels?

H. W. MCQUAID:[3] In this line of work the normal steels are the ones that the customer does not want and the steels which you usually have are the abnormal steels, and his normal steel is the abnormal steel, and everything is well reversed.

M. J. R. MORRIS:[4] There is a certain amount of work to be done in spheroidizing, and in one case we have to do all that by annealing in the simplest form, and in the other case we do it by help from the steel itself.

I cannot determine from the curve which is presented whether or not the time of four hours is enough to do the work at the temperature given. Sum-

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[1] *Metals and Alloys*, March, 1932.
[2] Chief metallurgist, Illinois Zinc Co., Chicago.
[3] Chief metallurgist, Timken-Detroit Axle Co., Detroit.
[4] Chief metallurgical engineer, Republic Steel Corporation, Central Alloy District, Massillon, Ohio.

marizing it simply, it certainly looks as though the one which has the greatest inherent tendency to divorce has certainly given help.

May I inquire whether the rolling was done cold or whether the strips were heated?

Authors' Closure

The authors wish to thank Dr. Rawdon for calling further attention to the fact that the abnormal steel is often the better steel to use, and that the use of the term "abnormal" is, perhaps, unfortunate. With reference to Dr. Rawdon's remarks concerning the 0.05 per cent chromium in the abnormal steel, it is true that the authors have considered this of no material import. However, the important factors brought to light in Mr. Bain's Campbell Lecture very clearly show that even smaller amounts of additional materials may influence the normality of the steel.

It is true that the Rockwell method of hardness testing yields doubtful results on very thin sections. The hardness determinations which were used in this paper represent, on the three final reductions, readings taken on multiple thicknesses of strip.

It is well to bear in mind that the testing of these sheets by the rolling mills, and also by their customers, is frequently done on single sheets as thin as 0.010 inch.

Mr. Epstein is somewhat in error regarding the properties of the "as-rolled" strip. It is true that the abnormal steel did not become as brittle as the normal steel, as indicated by the edge cracking. Nevertheless, the abnormal steel is the harder. The hardness of the "as-rolled" normal strips ranged from 101 to 105 Rockwell B, while the range of hardness in the abnormal steel is 104.5 to 108.

Some data are available concerning the comparative impact values of similar steels as well as normal and abnormal steels of 0.43 and 0.20 per cent carbon in substantiation of Mr. Epstein's remarks concerning the impact values.

With reference to Mr. Morris' question as to whether or not four hours is a long enough period, really what we have presented here is the major portion, but not all of the work which was done in this entire matter.

As a matter of fact, this experiment involves a series of steels annealed for four hours, and another series for eight hours, and another series for sixteen hours. When we had completed the work we laid out all the photographic results on a large floor, and after making a comparison between the four, eight, and sixteen hour anneals we thought we might just as well draw a line after four hours and stop it there, because there is really not anything to be gained by the longer time.

In answer to Mr. Morris may I say that the strips were entirely cold-rolled and there was no annealing whatever between passes. The only heat which we applied to them was the final annealing.

PRINCIPLES OF LUBRICATION IN COLD DRAWING SHEET STEEL

By H. A. Montgomery

Abstract

This paper deals with the principles of lubrication involved in the cold drawing, pressing and general shaping of sheet metal products. It also deals with the chemical and physical properties of natural lubricants utilized for this purpose, together with compounded lubricants generally furnished under secret formulae.

THE most important factor involved in the efficient production of metal stampings is, of course, die design and construction, but following next in order of importance is the matter of lubrication.

The extremely rapid development of the art of plastic cold working of metal has attracted in the past two or three years the attention of the lubrication chemist to this interesting field.

Efficient lubrication of production operations will effect a greater net saving to the average stamping plant than any other single factor, aside from correct tool design and construction.

Of the natural fats and oils sometimes used as sheet metal lubricants, those of outstanding merit are beef tallow, wool grease, lard oil, castor oil and elaine oil. Of the compounded lubricants widely furnished for this purpose, most of them will be found to be based principally upon the aforementioned fatty oils and fats, and, with few exceptions, are all prepared in the form of water-soluble emulsions, varying gradually from solid, pasty materials to viscous liquids. Such prepared compounds not only contain basic fatty lubricating material but also may contain varying quantities of mineral oils, the mineral oils usually ranging between 200 and 700 viscosity.

The principles involved in the lubricating of metal drawing operations have little in common with the principles involved in machine lubrication. The first and foremost requirement of a good cold drawing lubricant is high film strength, but it by no means follows that any

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A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, H. A. Montgomery, is president of the H. A. Montgomery Company of Detroit. Manuscript received May 26, 1932.

lubricant possessed of this characteristic is an efficient medium for the purpose.

Physical research has shown that a satisfactory lubricant must be properly balanced, principally as to coefficient of friction and surface tension. The apparent proper range of coefficient of friction, in accordance with physical research, is from 0.005 to 0.020. Surface tension in all instances should be as low as it is possible to obtain in any given lubricant. The factor of surface tension appears to be of the utmost importance, and those lubricants seemingly possessing the lowest surface tension, generally speaking, function most efficiently.

It is not difficult to fabricate lubricants possessing high film strength. This can be accomplished in several ways, and is usually controlled by increasing or decreasing the extent of saponification of the fatty bases, and or by the use of a solid lubricating material such as lead carbonate, calcium carbonate, talc, etc., introduced into the compound. Where cold cleavage or plastic flowing of metal takes place, lubrication is required of a different sort than is required in a machine bearing.

It has been found by long experience that certain lubricating materials, derived from fatty sources, possess inherent characteristics which seem to be lacking in lubricants derived from mineral sources. These properties, when developed by chemical treatment, are greatly enhanced in value as lubricants for this use.

We do not find lubricating mediums of natural occurrence satisfactorily answering the requirements of stamping plant usage. It is only by chemical process of compounding that we finally arrive at a balanced condition in a lubricating compound which fits the lubricating substance scientifically to the operation.

In the preparation of lubricants for general stamping plant use, certain physical conditions must be developed; dependent upon the perfection attained rests the merit or efficiency of the finished compound.

Generally speaking, these conditions are of a physical nature and establish definite limits as to choice of materials from which the lubricant may be compounded. While these conditions are principally of a physical nature, they are mostly arrived at through chemical treatment. The conditions referred to are as follows:

1. Highest possible film strength
2. Medium coefficient of friction
3. Lowest surface tension
4. Fixed solubility in alkaline and non-alkaline water
5. Oil solubility
6. Stability of the product
7. Toxic effect upon workmen
8. Proof against fermentation, decomposition or other chemical change
9. Proof against corrosion
10. Ease of application
11. Ease of admixing
12. Ease of cleaning
13. Odor and general cleanliness of use.

It will probably be of interest to mention the manner by which these specific conditions are arrived at in a given lubricant. High film strength is the direct result of choice of the basic ingredients, and the alkaline saponification of the fatty materials used. The extent of saponification determines to a considerable degree the ultimate film strength of the entire lubricant insofar as the oily body is concerned. The more of the fatty substance that is converted to soap, the higher the film strength will be. Coefficient of friction is established by control of the degree of water-solubility of the product, and the amount of moisture it contains as a component part of the entire formulation. Surface tension is controlled by proportioning the saponified and unsaponified oily bodies. Fermentation is controlled through the means of powerful chemical preservatives. It is extremely difficult to control, with guaranteed effectiveness, this matter of fermentation. Water emulsions, consisting of saponified and unsaponified fats and fatty oils, are apt to ferment readily under warm weather conditions in spite of all preservative precaution taken. Benzoic acid, when used in the proportions of one tenth of one per cent, is a most effective preservative, and gives the most satisfactory results of anything known at present. It has no toxic effect upon the workmen, and there are no known difficulties attendant upon its use. When all the foregoing conditions are met, a master lubricant results. No product may be considered wholly efficient that does not fully meet these specifications.

The principal function of a cold drawing lubricant is to prevent scoring of the work-piece or breakage of the metal during the drawing operations, as well as the prevention of excessive die wear. Under the high pressures developed in cold drawing and pressing operations, the film strength of the oily medium is usually exceeded, especially in the case of heavy duty work. When the lubricant film is ruptured, seizure of metal is likely to occur.

It is a physical impossibility to reach the required film strength of a drawing lubricant with any purely oily medium, saponified or unsaponified. It, therefore, becomes necessary to fortify the film strength of the oily medium with materials of a naturally tougher nature. This is usually accomplished by the addition of solid lubricating materials, in a finely divided condition, to the oily body of the lubricant, and the suspension of the same uniformly throughout the mass. These solids must be chemically inert so as not to affect the other ingredients of which the lubricant is composed. These solids must also possess natural lubricating properties. Their function is to aid in preventing metal to metal contact. The amount of such solid materials that may be added is limited, and usually forms from 20 to 30 per cent of the entire formulation. The amount of this material that may be used is limited due to the difficulty its presence imparts to the subsequent cleaning operations. They are not particularly effective in fortifying the film strength of the lubricant if used in lesser quantities than 20 per cent, and seldom form more than 35 per cent of the entire formula.

It is well to point out that, so long as more or less indestructible solid material is introduced between the metal of the work-piece and the die wall, a definite separation of metal to metal is maintained, and the chances of scoring are greatly reduced.

Solid lubricating materials added to the oily medium of a drawing lubricant are usually possessed of a high degree of oil absorption, and, due to this factor, are effective in carrying a definite portion of the oily medium directly between the metal of the work-piece and the die wall.

The pressures exerted during the drawing operation express the oily medium from the solid material, thereby maintaining some of the actual lubricating substance at a point where it is most required.

Generally speaking, the solid added to drawing lubricants is neutral calcium carbonates. There are other substances which may be added, such as lead carbonate, zinc oxide, barium carbonate, talc,

Fuller's earth, types of infusorial earth, types of clay and like materials.

Aside from the value of lead carbonate and zinc oxide, calcium carbonate seems to be most effective as well as the least expensive material which may be used. Lead carbonate and zinc oxide, while extremely effective as lubricating bodies, are chemically active in the oily medium, and have a marked tendency to produce water-insoluble fatty acid salts of these metals. This contributes a marked difficulty in cleaning, and, therefore, such substances are considered objectionable.

Calcium carbonate is practically inert, and possesses the required merits for this use. Talc is objectionable owing to its high abrasive properties. Barium carbonate is objectionable as it seems to influence fermentation. The clays are objectionable usually due to their high silica content. Further than this, calcium carbonate seems to be more easily cleanable than other substances.

Coefficient of friction of any given lubricant is a factor of small importance when considered from the standpoint of deep-drawn heavy metal stampings of small surface area. However, when considered from the standpoint of stampings drawn from light-gage sheet of great area, it becomes a factor of serious importance.

If the coefficient of friction is too low, the metal slips too freely into the die cavity, resulting in an unevenly drawn or wrinkled workpiece. If the coefficient of friction is high, breakage of the sheet takes place at the point of greatest stress.

Excessive adhesiveness of a lubricant also has a marked tendency to cause the sheet to open its grain structure, owing to the overstressing of the metal while drawing. Sheet metal having high percentage of stretcher strains is often affected by the adhesiveness of the drawing lubricant in use. In the preparation of well-balanced lubricating mediums for sheet metal drawing purposes, it is very necessary that the lubricant be accurately adjusted as to coefficient of friction.

Surface tension of good drawing lubricants should be low, due to the fact that lubricants, generally used for metal cutting and drawing purposes, are efficient or inefficient in direct proportion to their wetting properties. The wetting property of any given lubricant is of extreme importance, and this factor is reflected in surface tension.

Most cold drawing lubricants are prepared in the form of water-soluble emulsions. There are several reasons why they are so prepared. The principal reason is due to the dependence upon the soap

base of the lubricant. It is only by means of emulsification that the soapy materials can be uniformly dispersed throughout the unsaponified oily portion and maintained in that condition. Secondly, the suspension of the solid material is more readily accomplished and the compound is readily adjustable to various operations by water-dilution on the part of the user.

Solubility in alkaline solutions is desirable in the interests of subsequent cleaning operations. Stability against separation is an absolutely necessary requirement.

Drawing lubricants are sometimes compounded of materials that are toxic in effect upon workmen. This results in poisoning by absorption, and such conditions must be carefully avoided. Lead carbonate is particularly effective in this direction.

Color and odor of drawing lubricants must be not unpleasant. Color is of serious import when the lubricant is used on such stampings as automobile fenders, body panels, etc.

When such stampings are drawn, uniform lubrication does not take place on all sections of the draw ring. The lubricant is only applied to those locations on the draw ring where the metal is expected to flow freely into the die-cavity. At other locations on the draw ring, the metal is expected to hold with little or no movement. No lubricant is applied at those points. Definite color of the lubricant aids the operator in applying only where required.

There is not a great number of lubricating substances of natural occurrence that lend themselves readily for use as ingredients for efficient drawing lubricants, and no natural product known, which may possess merit in this direction, occurs in a suitable physical condition to permit its use efficiently or economically. It becomes necessary, therefore, to make a choice of those oily mediums which we know by experience to be best suited for the purpose. Two of the most important oily substances which form satisfactory bases for drawing lubricants are, in order of importance, beef tallow and castor oil.

Of the two substances, tallow, with an approximate film strength of 40,000 pounds, and a coefficient of friction of 0.005, is generally satisfactory in performance when used in its natural state as a drawing lubricant. Its film strength is considerably lower than that of castor oil, which is approximately 60,000 pounds, and its coefficient of friction is ten times lower than that of castor oil, but its wetting power appears to be much higher.

Therefore, if, as stated, the above two substances are effective

mediums from which to compound a good lubricant, it is desirable to take advantage of the higher film strength of the castor oil and the higher wetting properties and lower coefficient of friction of the tallow. The simple compounding of these two substances together does not result in a medium possessing proper physical conditions for economic and efficient use as a drawing medium.

However, by chemical treatment of these substances (by saponification, sulphonation and emulsification), we are enabled to take advantage of the peculiar characteristics of each. When they are so blended or compounded in correct balance, they produce truly remarkable lubricating results.

In the cold working operations of all metals, where such operations require lubrication, whether it be the cleavage of metal or shaping of it by plastic working, peculiar influences of lubricants are noted. It is a fact well understood by engineers and chemists that all metals, with the exception of aluminum, tool more readily and effectively under influence of lubricants derived from fatty sources.

It can hardly be stated that these influences are due to chemical action. They are more likely due to physical action or condition, but insofar as we can describe them, they are principally due to the wetting principle and film strength of the lubricant. We posses a fairly definite knowledge of these physical phenomena and effects, but other than supposing they are due principally to wetting power and film strength of the lubricant, we possess little other knowledge.

In late years we have noted the intensely efficient effect of sulphurized lubricating mediums. By sulphurization of mineral lubricants we are enabled to match, and in some instances surpass, the performance of lubricants derived from fatty sources. Sulphurized mineral oils are particularly effective lubricants on punching and shearing operations, and on short draws, and on heavy metal where the work-piece must be kept free from scores.

We cannot observe that the sulphurization of an oily medium increases its wetting power. We know that the thermal properties of the lubricant are affected by sulphurization, but this hardly explains their efficient performance. We are beginning to believe that perhaps there is chemical influence in some manner exerted, but nobody to our knowledge has offered a satisfactory explanation in this direction.

It has recently come to light that lubricating mediums, treated with chlorine or with chlorine-bearing compounds, are greatly enhanced in their lubricating performance. It is peculiar to note that the

introduction of such a volatile substance as carbon tetrachloride to an oily medium so fortifies its film strength as to make it well nigh indestructible when introduced into a machine bearing. This same influence is noted in a lesser degree when applied to lubricants for metal drawing operations. The peculiar effect of such chemical treatment of lubricants has set afoot interesting research, and we are noting with increased curiosity the effect of other corrosive substances when introduced into compounded oily mediums.

In very recent months we have been amazed at the performance of certain organic sulphates in compounded lubricants. We have recently witnessed the almost impossibility of the scoring of a sheet-metal work-piece, drawn under the influence of lubricants bearing minor quantities of these sulphates. Their use thus far, however, seems impractical owing to their corrosive nature. They may, however, prove extremely effective on the newer stainless metals. We have no data available in this direction at this time.

It is difficult to offer a satisfactory explanation of either a physical or chemical nature of these curious results. It seems evident, however, from recent research, that an entirely new theory in principle of lubrication will ultimately result—a theory which will attach considerable more importance to the chemistry of lubricants and less importance to the purely physical properties.

DISCUSSION

Written Discussion: By Joseph Winlock, chief metallurgist, Edw. G. Budd Manufacturing Co., Philadelphia.

Mr. Montgomery has prepared a very interesting paper on the requirements of a good lubricant for use in the deep drawing of sheet steel, and has described the effect of the different constituents on the properties of drawing compounds. I should like to add to the list of requirements which he has enumerated that of high heat conductivity. Sometimes, and especially in drawing metal of heavy gage, the amount of heat produced by the friction between the die and the metal being formed, and the amount of heat produced by the metal itself when being deformed, becomes very great. This may lead to excessive wear on the dies, and may also cause small particles of metal to adhere to the die ("die pick up"). The result of this is usually a severe scoring of the surfaces of the stampings.

It is hoped that Mr. Montgomery will continue his studies to include actual experimental data on the effect of different drawing compounds on given types of draws.

Written Discussion: By Maurice Reswick, chief engineer, Pennsylvania Lubricating Co., Pittsburgh.

Mr. Montgomery's excellent paper outlines concisely the essental require-

ments which a lubricant for cold drawing of sheet steel must meet and describes the influence of the ingredients commonly used in compounding such lubricants on the efficiency of operating performance.

Information of this kind is of great value to the industry, and it is a sign of progress when the cloud of mystery and secrecy which still surrounds this particular subject is being gradually dispelled. The engineer and shop superintendent is thus helped by the lubricant manufacturer to understand in intelligent scientific terms what the essential constituents are of a successful drawing compound, why they are used, and what function they perform.

On comparatively light drawing and stamping operations any oily, unctuous film adhering to the metal will serve as adequate lubrication. Slushing oils or soluble oils with which sheets are coated at the mill for preventing rust during shipment and in storage furnish sufficient lubrication in the mechanical processing of the material at the shop. However, as the depth or severity of the draw—and consequently the stresses involved—become greater, dependence can be placed only on lubricants possessing special properties of high film strength, provided the other equally essential requirements are not sacrificed unduly, and no harmful effects on the material worked or on the tools are introduced.

The usual types of greases used in the lubrication of machinery cannot be well adapted for drawing operations for the reason that they do not possess sufficient film strength, cannot be readily diluted, and are difficult to clean off. Drawing compounds, such as described by Mr. Montgomery, contain soap bases of mineral oils similar to those used in machinery greases, and the main difference between the two is the presence of an excess of free animal or vegetable fats or fixed oils in the drawing compound, together with an appreciable percentage of inert solid matter or fillers such as calcium carbonate (common chalk). It is largely the presence of free fat, usually in the form of tallow, that imparts greater film strength and increases the wetting properties or adsorption of the lubricant by the steel surface, as indicated in lowered surface tension of the lubricant.

While in a lubricating grease 2 or 3 per cent of moisture is considered as the maximum allowable, in order to bind the solid fillers and other ingredients of the drawing compounds together it becomes necessary to use as much as 20 to 40 per cent of water in their manufacture in order to produce a rich emulsion, approximating a gel, which retards—but does not entirely prevent—the settling out of the solids and the separation of the unsaponified oils.

Fermentation and its allied phenomena—rancidity, oxidation, discoloration, etc.—are all favored by the unbalanced chemical condition of the drawing compound, i.e., the existence of an excess of free fat in the presence of water, which creates an ideal setting for chemical activity particularly when the product is exposed to atmospheric conditions. Fermentation is a series of chemical reactions caused by micro-organisms which derive their nourishment from the unsaponified fats or from organic matter in general.

Preservatives, such as benzoic acid or cresol, act as a deterrent against fermentation, and while their use in connection with the described types of drawing compounds appears to be necessary, they should be regarded as an indication of manufacturing practice which is far from the ideal. In general, the

use of preservatives or scenting materials may cover a multitude of sins, even disguising the employment of inferior materials in the manufacture of the lubricant.

As to extreme pressure lubricants of the chlorinated sulphur type, our observation has been that their effectiveness in this direction varies directly with their corrosiveness, or the quantity of active chlorine and sulphur incorporated in the compound. The nature of the film which prevents scoring in lubricants of this type does not depend so much on the "oiliness" of the compound as it does on the formation of a minute layer of chemically reacted iron sulphide or chloride over the surface of the work-piece and the die on which the compound is spread. The corrosiveness of such compounds, of course, rules out their extended use.

As manufacturers and marketers of extreme pressure lubricants, we have found that when lead oleate, commonly known as lead soap, of the proper degree of purity is incorporated in a blended oil with which it is miscible or incorporated in special compounds and grease, the resulting products possess all necessary extreme pressure characteristics without entailing any objectionable features such as corrosion, abrasion and staining.

Oral Discussion

JOHN R. DAESEN:[1] Mr. Montgomery is to be congratulated for his paper on a subject that has not had a great deal of attention in our technical literature. It is particularly important to producers of the new nonferrous sheet metals.

In the past, steel and brass have been used almost universally for stampings, and a good many lubricating solutions have been made up, perhaps by rule of thumb methods which those in the business know from long experience will work, but when a new metal is used, very often it takes a long time to find the proper lubricating solution that will give the best results. For that reason a technical consideration of the various elements that are concerned with lubrication will prove very valuable in the introduction of new alloys for forming work.

In particular connection with this point is the consideration of the mechanism of the wetting. The theory has been expressed from several points that wetting results only when there is some chemical action between the lubricant and the metal.

In that connection, it will be readily apparent that if we are going to draw an alloy of zinc, for example, a corrosive medium in the lubricant which gives just the right amount of wetting with steel might be entirely too corrosive for drawing the alloy of the more readily corroded metal.

I think that further work on this subject would be of more universal value if, in addition to considering the nature of the draw, the nature of the material were considered and different lubricants developed that would be adaptable to these different newer metals because of their different chemical properties.

M. J. R. MORRIS:[2] I would like to ask Mr. Montgomery if he has, in his

[1] Chief metallurgist, Illinois Zinc Co., Chicago.

[2] Chief metallurgist, Republic Steel Corporation, Massillon, Ohio.

experience, observed whether it is advisable at times to especially pay attention to the condition of the surface of the product which he is going to roll. I have in mind extremely heavy draws and stainless steels.

We have lived through a tremendous lot of experience on stainless steels, and we have called upon the help of all the experience which went ahead. We have made many mistakes. When we had a product with ample ductility, in fact double that of the regular product, we obtained poor results. In plain English, we did not know how to use the ductility which was at our disposal.

I think the work done by Mr. Montgomery has helped the industry tremendously.

I would like to ask Mr. Montgomery if he found the characteristics of the surface of outstanding importance; in other words, could it make or break the application of the compounds used?

What I am unable to clear in my mind is, should we use a solid lubricant in certain cases or should we use a dual lubricant where you have emulsion, and help that to function by a solid lubricant on the surface of the job being drawn.

H. W. McQuaid:[3] There is one thing I would like to say. In this lubrication of cold drawing in gears, or lubrication of anything, the important thing is that the lubricant, particularly in cold drawing, has to be stronger than the material itself. I do not mean stronger than a die, but stronger than the softest of the two materials.

I have done a lot of work in the last year on lubricants of all kinds, particularly in conjunction with scoring, etc., and I know, for instance, that the pressures of gears are much greater than the pressures that we get in cold drawing sheets or solid bars, even though we do not usually consider them so.

The question of wetting the surface is an important one. The use of lard oils and castor oils and non-mineral oils in conjunction with mineral oils does increase this wetting, but the addition of sulphur or chlorine or sulphur chloride to lard oil does develop lubricants with tremendous film strength, which satisfy every requirement of actual film strength.

It has been our custom to use white lead and castor oil in deep-drawing, and apparently there has not been any great improvement, as far as I can learn from reading these papers, in the materials we have been using, outside of your E. P. lubricant, but there seems to be in this paper a consolidation of ideas as to the proper lubricants for sheets.

Author's Closure

There is some considerable bearing upon the performance of a lubricant from the standpoint of surface conditions of metals to this extent—we find, through many years of actual experience, that cold-rolled sheets are extremely difficult to keep free from scoring. Where we have hot-rolled and pickled sheet, where the grain surface is open, it seems that the drawing lubricant will adhere better to the sheet and perform better than when applied to the finish of the cold-rolled sheets.

It has been said that the cold-rolled sheets have a soft skin on the outer

[3]Chief metallurgist, Timken Detroit Axle Co., Detroit.

surface that causes most of the trouble. There apparently is no difference in the performance, from the standpoint of breakage of the sheet, between cold-rolled and hot-rolled, but there is a considerable difference from the standpoint of scoring. There is markedly more scoring in a cold-rolled stamping than a hot-rolled one. We never have undertaken to produce special lubricants for it. There is no particular reason for our not having done so—we just have not.

We are more or less successful with the products which we have already made for general stamping purposes. They work quite efficiently, but cold-rolled steel does give us more trouble from the standpoint of scratching and scoring.

The best answer I can give to Mr. Morris' question is that we use a solid lubricant. The cross section of the stamping has a great deal to do with the type of lubricant. When the stamping is heavy and the pressures are heavy it is necessary to fortify the film strength of the lubricant with more of the solid material. When we come to the light gage metals, especially on deep draws and small sectional areas, good results can be obtained by simple soap or oil emulsions, or oily mediums themselves that run high in saponifiable fats or oils.

On the heavy cross sections we must use pigments. It is necessary to resort to some such material to gain the proper film strength.

That is not wholly true. In answering Mr. Reswick's discussion I bring out the point that we have a distinct demarcation between the lubricants as they are prepared for general use. One class takes in emulsions of both soluble and insoluble nature, and the other class takes in either chlorinated or sulphurized products. Usually the emulsified products are used on light gage sheet metals, and the chlorinated ones are used on the heavy cross sections where the draw sets up extreme pressures.

The sulphurized products seem to function more efficiently and take better care of the heat that develops. When we use sulphurized oils we do not generally pigment those products or use any solid lubricant. We depend on chemical properties to take care of the entire operation.

In reply to Mr. McQuaid's reference to the use of white lead and castor oil, I do believe that God never put on the face of the earth anything that was more effective than white lead or castor oil. It forms the strongest film strength of anything we have had to contend with, but there are objections to the use of white lead. You cannot clean it off and it has a toxic effect on the workmen. Many men are susceptible to lead poisoning, so the use of lead carbonate or lead oxide is about ruled out. You find its use very limited today.

We can approach quite closely the merits of white lead and castor oil by these prepared compounds, and we seem to be able to perform most of the requirements of those lubricants.

In replying to Mr. Reswick's discussion of my paper I am not prepared to admit that the use of preserving and scenting materials should be regarded with suspicion by the user of such lubricants as I have described.

He may be somewhat justified, in my opinion, to the end that such additions may be used to mask the use of inferior ingredients. However, the de-

mands of present day stamping plant practice are so severe upon lubrication performance that it is unlikely a manufacturer of these highly specialized lubricants could attain the required efficiency should he resort to the use of inferior materials.

Such products containing unduly large amounts of water may be justifiably regarded with suspicion but an experience extending over some fifteen years of time has failed to indicate any satisfactory methods other than emulsification by means of which a more or less universally satisfactory product for this use can be compounded and held uniformly together. The presence of an appreciable volume of water in a lubricant such as I have described is essential but it should not exceed 20 to 25 per cent of the formula. Beyond that it amounts purely to adulteration unless there is special reason for an excess amount.

The presence of such a volume of water in these products is the basic cause of fermentation and allied phenomena as mentioned by Mr. Reswick. Therefore, so long as I, a manufacturer of such products, am aware that my product is subject to the condition of fermentation I hold that I may take every precaution to guard against the condition without being subject to question as to my motive in making use of chemical preservatives.

Scenting materials are not nearly so often used to mask the odor of inferior materials as they are used to confuse an analyst or cover an objectionable odor that may find its source in a perfectly clean and wholesome ingredient.

In this connection I mention common degras or commercial wool fat which is extensively used as an ingredient in drawing lubricants due to its peculiar emulsifying characteristics and lubricating properties. It is a clean and wholesome fatty material. Its natural odor is somewhat unpleasant and when saponified the odor is considerably intensified. The odor does not spring from putrefaction or any allied cause; it is due to the character of its free fatty acids. I again hold that as a manufacturer making use of the desirable properties of such an ingredient I am justified in masking its odor.

Mr. Reswick, in his discussion, mentions the use of lead oleate to attain required film strength in an oily preparation for use as a drawing lubricant.

The value of metallic soaps in this connection has had considerable attention on my part, for while their use does lend considerable film strength to lubricants I have observed that such compounds possess only mediocre merit as sheet metal production lubricants. We have observed that lead oleate in particular has a marked tendency to support emulsions of such compounds against separation.

As to Mr. Reswick's reference to the effectiveness of the so-called corrosive lubricating compounds I agree that such compounds are effective somewhat in proportion to their corrosive activity. They should not, however, in my opinion, be ruled out entirely as they may be used most effectively upon many classes of heavy stampings where their comparatively slight corrosive action is of no importance. This is particularly true in connection with the sulphur-bearing variety where the merit of the product is dependent upon a natural mercaptan content or sulphur in solution. In these instances the value of the sulphur ingredient is lessened but the corrosive action, if any, is so slight as to be of no detrimental importance.

In Mr. Winlock's discussion of my paper he sets forth the desirability of high heat conductivity in a good drawing lubricant. I agree with Mr. Winlock that the thermal properties of such lubricating media should not be overlooked and have not been.

As Mr. Winlock has pointed out, the heat developed in a drawing operation comes from two causes; that is from the friction of the metal passing over the die wall and from the internal friction within the metal being worked.

A satisfactory lubricant should and does reduce the former but probably has little influence upon the latter, as most drawing operations are surrounded with such a small volume of lubricant that the lubricant present can only absorb a fraction of the heat set up from internal friction.

I would point out, however, that a marked difference in thermal conditions is noticeable between metal parts drawn with soap base emulsified compounds and those drawn with the so-called corrosive lubricants and it is much in favor of the corrosive lubricant, and it is particularly so in connection with the sulphur-bearing lubricants. I can offer no reasonable explanation for this phenomenon.

On a recent experiment a metal part weighing 5¾ pounds, taken directly from the draw die and placed in a fixed volume of water showed a difference of 23 degrees Fahr. in the amount of heat absorbed by the water in a given time period. In one instance the part was drawn using an emulsified soap base lubricant and the other using a corrosive lubricant. Both lubricants were producing satisfactory results insofar as scoring was concerned.

AGE HARDENING IN LOW CARBON STRIP STEEL

By Earle B. Whittemore

Abstract

This paper discusses the phenomenon of age hardening in low carbon strip steel. General specifications are given for the physical properties of cold-rolled strip for the various uses in industry.

Aging is a condition of definite increase in hardness, elastic limit and tensile strength with a consequent loss in ductility or workability occurring during the period when the steel is at rest at normal temperatures following the completion of cold work.

The results of many tests under standard mill conditions are shown in a table form as well as in curves.

A brief discussion of the effect of carbon content on the aging characteristics is given.

MANY users of low carbon cold-rolled strip steel have shown considerable interest in the increase in hardness and loss of ductility due to aging in basic open-hearth steel of the following composition: Carbon, 0.05 to 0.15 per cent; manganese, 0.30 to 0.50 per cent; phosphorus, 0.05 per cent maximum; sulphur, 0.05 per cent maximum; and silicon, 0.05 per cent maximum.

Whereas most manufacturers and consumers of this type of material accept age hardening as a fact, they do not agree upon the extent of the increase in hardening. This may be due in part to a failure to mention the *temper* of the material in question and the *period* of aging.

At the outset let us define "temper." Temper of cold-rolled strip steel indicates the degree of hardness and the ductility best adapted for further work (such as blanking, forming, perforating, or drawing to shallow or deep cups and tubes). These different physical properties in low carbon basic steel (cold-rolled strip) are obtained by controlling the amount of cold rolling done upon the hot-rolled material or on the material in the soft or annealed state.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author was associated with the Wickwire Spencer Steel Co., Worcester, Mass. Manuscript received July 30, 1932.

Tempers are designated by terms from "full hard" to "dead soft"—numerically from number one (full hard) to number five or six (dead soft) for deep drawing. In more recent years Rockwell and Brinell hardness tests have been of great assistance to strip steel manufacturers in supplying material within close limits of hardness. General specifications are given in Table I, wherein plasticity is noted as elongation in a standard tensile test piece. Ductility—so-called—is a physical property overlooked by many consumers, and may be

Table I

General Specifications for Basic Open-Hearth Low Carbon Cold-Rolled Strip

Temper	Rockwell Hardness	Arbitrary Temper Index	Minimum Tensile Strength Lb. per Sq. In.	Elongation % in 2 In.	Notes
Hard	B-90 and over	1	60,000		Flat work and easy punchings. No bends.
Half Hard	B-75 to B-90	2	55,000	Min. 5, Max. 20	Easy blanking. 90° bend across the grain.
Quarter Hard	B-60 to B-75	3	45,000	Min. 15, Max. 39	Medium soft. Bend 180° across the grain, 90° with the grain.
Soft	B-50 to B-60	4	40,000	Min. 39	Bending, forming, shallow drawing. 180° bend either way of the grain.
Dead Soft	Under B-50	5 or 6	40,000	Min. 40	Extra deep drawing quality.

determined by one of several ball and plunger testing machines which form a cup under known conditions of load and depth of draw. When he specifies a Rockwell or Brinell hardness value and a cupping or drawing test, the consumer of strip steel has made known his definite requirements.

Much has been written and said about the limits which should be written into various specifications for materials. Much of this also applies to cold-rolled strip steel. The hardness range (as determined by the Rockwell method) considered by the writer to be liberal to both consumer and manufacturer for a given temper range, is about ten points on the B scale using the 100-kilogram load with $\frac{1}{16}$-inch steel ball penetrator on thicknesses of 0.020 inch and heavier. Thinner sections should be tested under the 60-kilogram load and the hardness range slightly reduced, whether the material is to be used for blanking, forming, perforating, or drawing by full-automatic, semi-automatic or manual feeding methods.

Table II

Aging of Basic Open-hearth Strip Steel

Rockwell Hardness at Time of Rolling	Expected Increase in Hardness		
	5 Days	30 Days	7 Months
B-40 to B-50	1 to 2 units	2 to 5 units	6 to 7 units
B-50 to B-60	3 to 4 units	4 to 6 units	7 to 8 units
B-60 to B-70	3 to 4 units	6 to 8 units	7 to 8 units
B-70 to B-80	3 to 4 units	4 to 6 units	7 to 8 units
B-80 to B-90	2 to 3 units	4 to 5 units	5 to 6 units
B-90 to B-100	1 to 2 units	2 to 3 units	2 to 3 units

Although manufacturers may adhere strictly to a hardness range similar to the above, discrepancies will be noted between the hardness readings reported by the consumer upon receipt of the strip steel and the testing records of the manufacturer of the same shipment of material. Incidents of this kind have brought about a more common recognition of the phenomenon of age hardening, which the writer will now attempt to present briefly for practical application by readers interested in the changing physical properties of steel of the above analysis.

Aging is a condition of definite increase in hardness, elastic limit, and tensile strength with consequent loss in ductility or workability. It occurs during the period the steel is at rest at normal temperatures following the completion of cold work. This phenomenon has been recognized in many metals and alloys, both after quenching and after cold deformation. Many researches have been carried on, both here and abroad, to determine its causes and possible control.

The extent to which basic open-hearth steel, in the form of low carbon cold-rolled strip, ages under normal conditions appears to cover a considerable period of time, although it becomes noticeable about five days after rolling is finished. The results of many tests made under standard mill conditions are assembled in a curve (Fig. 1) and in Table II. The curves show the average increase in Rockwell units; the data include all tests for periodic increase in hardness taken at various times during the past two years. The table indicates the expected increase in Rockwell hardness units within definite periods. The samples were taken during the production of various thicknesses, and were not control samples for a laboratory investigation. This method was used to secure averages which would be applicable to general mill practices and which would not be dependent upon any particular type or method of cold rolling procedure.

Tests on annealed material are erratic. Some aged only slightly

within one month and showed a marked increase thereafter. Other annealed material followed the same general increase as medium tempers, although the increase was much slower.

The greatest amount of aging was found in tempers of a Rockwell hardness B-50 to 80; increases of some samples reached 10 to

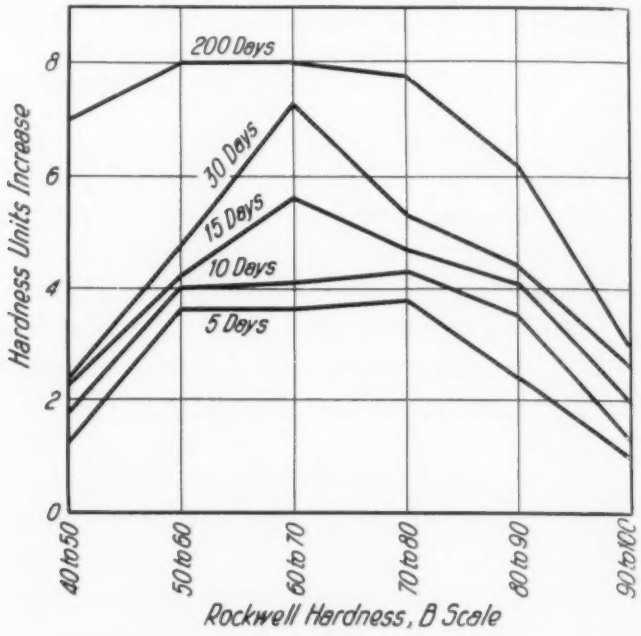


Fig. 1—Increase in Hardness Due to Aging of Low Carbon Strip Steel, Cold-Rolled by Commercial Mill Practice.

11 points on the B scale during the seven-month period. Harder tempers, B-80 and higher, seldom hardened more than 5 or 6 points during this period of time.

Some rather interesting additional observations have been made during these tests which, although known to science for some time, have not been given general recognition. While annealed material appeared to age more slowly and with erratic results, when subjected to a "pinch pass" (very slight reductions of 0.0005 to 0.001 inch, depending upon the thicknesses being worked) this material is subject to moderate aging. It also appears that the speed at which the aging takes place is related to the amount of cold work in reduction from the annealed condition. The rate of aging is larger in some tempers—aging requires more time for the harder tempers than for the softer tempers, and the soft and medium tempers age to a greater extent within a specified time.

Apparently, cold working in various degrees intensifies or retards the practical evidences of aging, within limited periods. If annealed strip 0.020 to 0.060 inch thick is reduced 0.002 inch by cold rolling, aging becomes more rapid and pronounced. This probably accounts for the similarity of aging in the soft and medium tempers.

If the material in the annealed state has a Rockwell hardness above B-50, the annealed hardness does not influence the aging which readily responds after cold working. Most material in these tests had an annealed hardness under Rockwell B-45 (many under B-40) which accounts for the great increase in hardness of the medium tempers after prolonged periods of rest. (All tests recorded in the B-40 to B-50 hardness range have been subjected to cold working. The hardness ranges above B-50 are developed by varying amounts of reduction by cold working.)

Several hard samples of cold-rolled steel of medium and high carbon content (approximately 0.60 and 0.90 per cent carbon) were also tested and found to age harden only to a slight degree, say 1 to 3 points, and then only after at least one month at rest.

It has been recognized for some time that age hardening may be accelerated by subjecting the material to temperatures of 200 to 600 degrees Fahr. For practical application, immersion in boiling water from 15 to 30 minutes will indicate the extent of aging for one or two months under normal conditions of material at rest.

Several theories have been advanced by scientists to explain this phenomenon of aging. Aging or seasoning is evidently a property possessed by many metallic alloys. Duralumin is a conspicuous example. Perhaps the most widely accepted explanation is known as the precipitation hardening theory, which postulates a supersaturated solution retained at room temperature from which particles gradually precipitate, causing an increase in hardness. The theory agrees with the more recent iron-carbon equilibrium diagrams, which show a slight solubility of carbide in alpha iron from room temperature to approximately 1700 degrees Fahr. This theory has been strengthened by investigations on hardness changes in quenched low carbon steels, although conflicting opinions exist as to whether the precipitation of small particles causes hardness, or whether hardening is due to a rearrangement of the space lattice resulting from the precipitation.

The effect of carbon on the age hardening capacity of steel has

received considerable attention. Low carbon steels containing approximately 0.0025 per cent carbon appear to age only to a negligible degree after cold working. Steels with intermediate carbon content up to 0.14 per cent have been reported to age in varying amounts consistent with the increased carbon.

Others believe that the oxygen content, either as oxides or dissolved oxygen, has a determining influence. Developments in science appear to show that an increase in the oxygen contained in low carbon steel enlarges the area in the iron-carbon equilibrium diagram within which carbide is soluble in alpha iron. This lends further evidence to the theories of precipitation hardness. Nitrogen, copper and other elements have also been suggested as exerting a possible influence on the extent of age hardening in low carbon steel. Considerable evidence has been produced to substantiate the above theories, although definite agreement as to the causes of age hardness has, to the writer's knowledge, not yet been secured, as much research in this field is yet to be completed.

In concluding this brief discussion of the ability of low carbon steel to change in physical properties following cold working, it should be apparent that specifications for cold-rolled or cold drawn material of a carbon content under 0.15 per cent should make allowances for aging or seasoning. With the increasing amount of information becoming available on the subject, slight changes in hardness, tensile strength, elastic limit, elongation and yield point may be determined with more accuracy. Greater recognition should be given to the changed properties of this type of material at the time of further fabrication, rather than at the time of manufacture, since the consumer usually has the most information concerning the amount of workability which this type of steel should possess.

AUTOGRAPHIC STRESS-STRAIN CURVES OF DEEP-DRAWING SHEETS

By Reid L. Kenyon and Robert S. Burns

Abstract

A description is given of the design and manipulation of an autographic apparatus for drawing stress-strain curves for sheet tensile specimens. A special curve-measuring ruler and its use is also described. Tensile stress-strain curves obtained with the new autographic attachment are shown, some of which give an experimental confirmation of the theory that the sharp yield point in mild steel is related to stretcher-straining. A method is developed for computing the depth of the stretcher-strains from the amount of elongation through the yield point. Curves are given for sheet material that has received various percentages of cold rolling. True stress curves have been constructed from autographic stress-strain curves of sheet samples and these are discussed briefly.

The stress-strain curve is shown to furnish considerable information concerning the behavior of deep-drawing sheet material in addition to that obtained from the ordinary tensile test. The yield point elongation and the uniform elongation are specific examples of significant values that can be determined only from accurate autographic stress-strain curves.

Introduction

ONE of the most commonly used methods for measurement of the physical properties of metals is the tensile test and it is, therefore, quite natural that it has been applied to the study of sheet metal for drawing purposes. While several papers (1),* (2), and (3), have been published on the tensile testing of sheet metal and its application to deep drawing sheets, reliance has been placed solely on the numerical values obtained from the test, that is, the yield

*The numerals appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The authors are members of the society and are, respectively, supervising research engineer and research engineer of the American Rolling Mill Company, Middletown, Ohio. Manuscript received June 15, 1932.

point and the tensile strength, and the per cent total elongation based on some definite gage length (generally two or eight inches).

Except for the work of several investigators on heavy plate and machined-round specimens, there has been little work done on the actual interpretation of the stress-strain curves obtained in the tensile test; numerous papers have been published, (4), (5), (6), (7), and (7a), on this subject, but none of them have dealt with stress-strain curves of thin sheets tested in tension. Crane (8) has applied the theory developed by Sachs (9) and other German investigators to the study of the deep drawing problem, but has published no experimental stress-strain curves on sheets.

Stress-strain curves of sheet specimens are similar in appearance to those of other shaped specimens of the same material and the general characteristics of such curves are described in most books on strength of materials. While it is possible to construct stress-strain curves by plotting corresponding values of the two variables point by point, it is much more satisfactory to use an autographic recorder which will draw a continuous curve. Only by the latter method can the more minute and in many ways the more important features of the curves be obtained. For this purpose various forms of apparatus have been devised; in general, however, these are so troublesome that for the majority of tensile tests made at the present time, stress-strain curves are not drawn, but merely the yield point, tensile strength, and per cent elongation are determined.

There are many difficulties involved in making autographic stress-strain curves on sheet tensile samples; these are particularly severe if the autographic device must be simple enough in operation to be useful in routine testing. In attempting this, the authors found the regular extensometers not sufficiently accurate and accordingly developed new extensometers and a special technique for drawing accurate stress-strain curves. From a study of such curves it has been possible to work out derived values which are thought to have some usefulness as measures of drawing quality of sheet materials. This paper describes the special equipment and the technique which the authors have developed, and includes some interpretation of the curves obtained.

Description of Standard Equipment

An Amsler hydraulic universal testing machine was used in all

of the work, principally because of its adaptability to the use of autographic attachments. This machine comes equipped with a recording drum and a pen arm directly connected to the load-measuring device (pendulum dynamometer). The pen arm plots the load in pounds and the rotation of the drum plots the deformation in inches. The load and deformation scales can be varied independently within certain limits. The rotation of the drum is accomplished by means of a cord which is connected either to the moving head of the machine

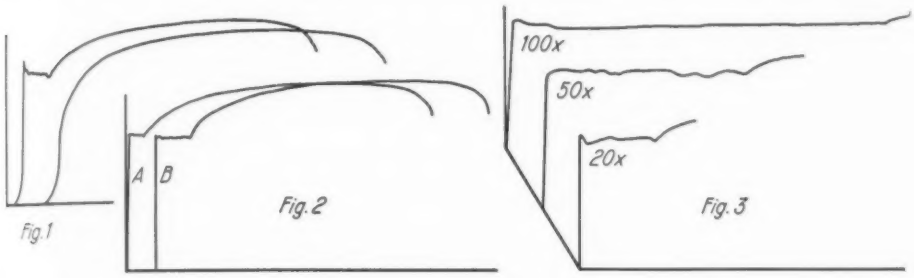


Fig. 1—Curves Drawn with Heads of Testing Machine Acting as Extensometer.
Fig. 2—Curve A Drawn with Standard Extensometer and Curve B Drawn with Wedge Extensometer.
Fig. 3—Curves Drawn with Screw Extensometer at Various Magnifications as Indicated.

or to an extensometer which clamps on the specimen. In the first method the head moves a greater distance than the sample elongates due to the pulling-in of the wedges and the taking-up of slack in the system. This causes the curves to be too long. Fig. 1 shows two curves drawn by this method, and it will be seen that the elastic portion of the curves is not the straight line it should be. All parts of these curves are inaccurate, however, because the elastic deformation of the entire straining system of the testing machine is added to the total deformation of the sample.

The second method employs the same principle as the first, except that the movement is taken between the two ends of the gage length of the sample instead of between the two heads of the machine. This is accomplished by a special form of extensometer consisting of two parts which clamp onto the two ends of the gage length of the specimen and which are so constructed that they are pulled apart as the sample elongates. In this arrangement the cord is fastened to the upper clamp and passes over a pulley on the lower one, and then, after passing over suitable guide pulleys, is wrapped around the recording drum on the dynamometer. A weight on the lower end of the cord keeps the tension as nearly constant as pos-

sible, although the elastic stretch of the cord is one source of trouble. As the sample elongates the cord is pulled and the drum rotated. Experience has shown that this method also leads to inaccurate curves, curves which are generally too short. This may be due to the difficulty of getting constant tension in the cord or to the inertia effect in starting the weights moving upward against gravity as the sample starts to elongate. At any rate, the elongation at the yield point is always found to be greater than the curves indicate, and the total length of the curves is therefore less than it should be. Fig. 2 shows duplicate specimens pulled under the same conditions except that curve (A) was drawn with this type of extensometer and curve (B) with the wedge extensometer, which will be described later.

Description of New Equipment

After drawing a large number of curves with the ordinary extensometer, it was apparent that greater accuracy was necessary in order to study the relationship between stress and strain in the tensile test. Experiments were accordingly conducted leading to the development of two different instruments, which have proved to be capable of producing accurate stress-strain curves on the Amsler machine. With both of these new extensometers, the elongation of the sample is magnified by the extensometer itself and this magnified motion transmitted to the drum by means of the cord. Another point of difference between these two new instruments and the standard extensometer is that the cord moves away from the extensometer, thus allowing the weight to move always downward. This tends to keep a more constant tension in the cord.

One of these new extensometers based on the screw principle is similar to one described elsewhere[1] (though developed independently) except that it is made for 2-inch gage length specimens and that the magnification can be varied over a wider range. As the sample elongates the two halves of the extensometer are separated, the micrometer follows up this movement and the motion of the cord occasioned by the rotation of the screw is transmitted to the recording drum of the dynamometer. It has been found difficult to design this extensometer to get magnifications that are small enough to permit the drawing of the entire stress-strain curve on the usual size recording drum. Its greatest value is in drawing an enlarged portion

[1] *American Machinist*, September 13, 1930.

of the curve to show the behavior of the material as it passes through the yield point.[2] Fig. 3 shows three curves drawn with this extensometer at various magnifications as indicated.

The most desirable magnification for drawing stress-strain curves of an entire tensile test is that which produces as long a curve as can be drawn in one revolution of the recorder drum. With the standard Amsler equipment the best magnification for specimens of 2-inch gage lengths is 10 times. The extensometer shown in Fig. 4 was finally developed for drawing the entire stress-strain curve and endeavors for patent protection on it are being made. In principle it is similar to the screw extensometer, for it also measures the movement between the two parts of the extensometer which are fastened to the two ends of the gage length. It differs from the former in that a wedge takes the place of the screw. This wedge works between grooved rollers on the two halves of the extensometer in such a way that it is constantly in contact with the rollers. A weighted cord passes around the recording drum and is fastened to the small end of the wedge which moves forward as the sample elongates, since the weight on the end of the cord keeps it constantly in contact with the rollers on the two halves of the extensometer.

Manipulation of Wedge Extensometer

In order to draw accurate stress-strain curves it is necessary to use the proper technique as well as the proper equipment. The description of the technique will be limited to that which has been developed for using the wedge extensometer with the Amsler testing machine.

Special self-aligning wedge grips, such as those developed by R. L. Templin, should be used in order to insure uniform loading of the samples. A piece of paper is placed on the recorder drum, the zero position of the pointer adjusted, a specimen placed in the grips, the extensometer attached, and the cord[3] run over the pulleys in the proper manner. The specimen and grips are turned (this applies to

[2] R. L. Templin has recently (American Society for Testing Materials 1932 Preprint No. 89 presented at the Thirty-fifth Annual Meeting, June 20-24, 1932) described an automatic autographic extensometer for obtaining load-strain curves at strain magnifications from about 400 to 16,000.

[3] It is important that the cord be of a weight and quality that will have the least stretch. It has been found that a fish line of the following specifications is satisfactory: Shakespeare's Wexford close braided, super waterproof, super silk casting line. Test 30 pounds. Made by Shakespeare Company, Kalamazoo, Michigan.

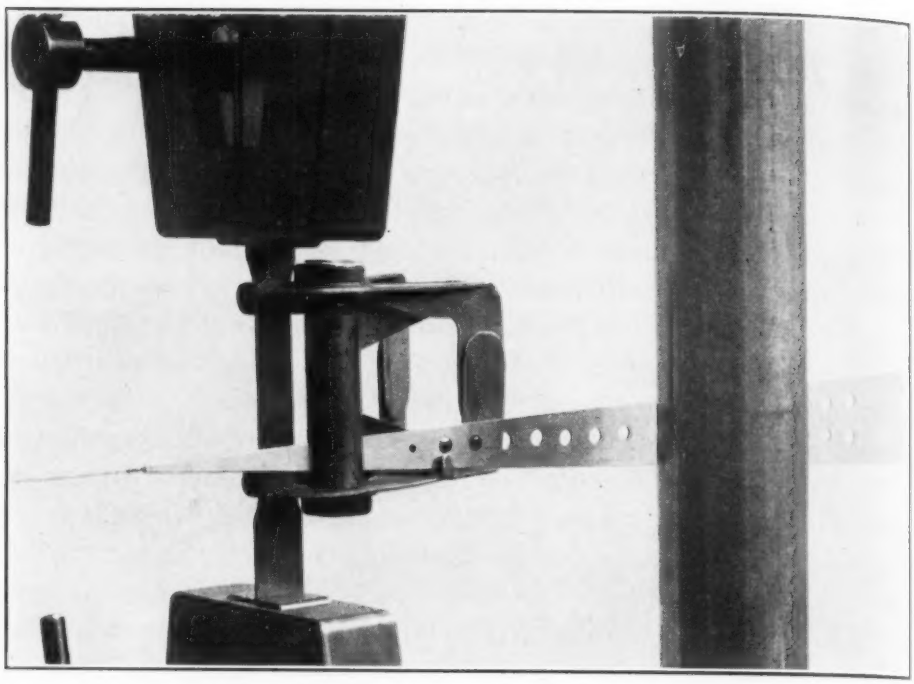


Fig. 4—Wedge Extensometer Developed for Drawing Entire Stress-Strain Curves of Sheet Specimens.

the Templin grips) so that the cord and the wedge are directly in line. The crank on the lower cross head is now turned slightly and a small load applied to the specimen. This is to set the grips on the sample and should be only about 100 pounds, except that in no case should it exceed 50 per cent of the yield point load. Care should be taken to see that the tension in the cord is correct, i.e., that it is the same at the start as it will be during the test. The cord should not be pulled too hard because the 10:1 leverage of the wedge may spread the two halves of the extensometer on the specimen. A Barch-Payzant No. 7 or 8 lettering pen[4] is much better than a pencil for recording the curves and should be supplied with a small amount of Higgins' Eternal Ink which does not dry in the pen as rapidly as Higgins' Waterproof Ink and seems to work much better. The extension arm on the pendulum (which moves the threaded rod on which the pen is fastened) is held back with the left hand until the pointer on the scale reads zero. The pen is then lowered to the paper with the right hand, the left still holding back on the pendulum. The right hand gradually opens the needle valve to the proper point for

[4]Manufactured and sold by Keuffel & Esser, New York City.

the desired rate of strain below the yield point (10). Simultaneous with the opening of the valve and the beginning of loading, the left hand should allow the gradual release of the pendulum. If this is properly done, the pendulum will not surge, but the load will be picked up gradually, as indicated by a regular advancing movement of the pointer on the dial. Otherwise, the pendulum will surge and

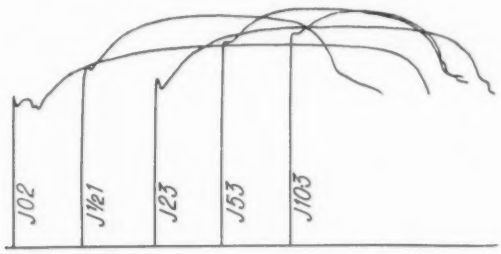


Fig. 5—Reproduction of 5 Stress-Strain Curves Drawn with the Wedge Extensometer.

Table I

	Sample Number				
	J02	J½1	J23	J53	J103
W_o	0.5015	0.5015	0.5015	0.5005	0.5025
T_o	0.0495	0.0500	0.0485	0.0472	0.0438
Y.P. #					
Upper	762	905	840	....	....
Lower	702	890	785	1025	1072
T.S. #	1017	1155	1108	1197	1188
Sample					
Lf	2.84	2.49	2.63	2.45	2.31
%El. Total	42.0	24.5	31.5	22.5	15.5
Y.P.-#/in.^{2}					
Upper	30,700	36,100	34,500	.....	.....
Lower	28,300	35,500	32,300	43,400	48,700
T.S. #/in.^{2}	40,950	46,050	45,600	50,650	54,000
El. Ra. (L)	0.690	0.771	0.708	0.856	0.903
Curve					
%E.-Y.P.	3.3	1.0	1.3	1.0	1.0
%E.-Unif.	27.5	13.5	17.0	8.0	6.0
%El.-Total	41.7	24.9	32.5	22.5	16.0
Type	A-2	C-3	C-3	B-5	B-5

if one of the surges coincides with the yield point, the indicated and recorded value for this quantity may be considerably in error. As soon as the load begins to rise again after the yield point is passed, the valve should be opened to the proper setting for the rate of strain to be used above the yield point (10). This should be done rather slowly in order to minimize any irregularities in the curve due to change of speed.

Different specimens will show wide differences in their elongations and their curves will therefore occupy spaces of varying size

on the paper; the number that can be drawn on one sheet will therefore vary somewhat. One of the important points on the stress-strain curve is the maximum load and the spacing of the curves on the sheet should be such that they do not overlap or intersect near this point in such a way as to obscure it. This is especially true if the

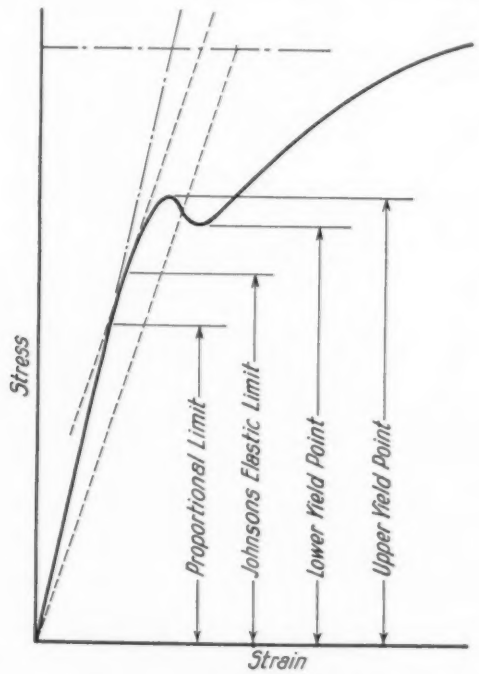


Fig. 6—Illustration of Definition of Proportional Limit, Johnson's Elastic Limit, Lower Yield Point, and Upper Yield Point.

uniform elongation is to be measured. Fig. 5 is a reproduction of five stress-strain curves as drawn with this extensometer. Table I gives the total elongation values obtained from the measurement of the samples and the curves and it will be seen that these check within the accuracy with which the gage length of the samples can be measured, and furnish a verification of the accuracy of the extensometer.

Definition and Determination of Values

Before discussing the interpretation of the stress-strain curves it should be pointed out that when such curves are drawn autographically, they have no standard scale for unit stress due to the variation in cross section of different test pieces. This makes it difficult to compare curves from samples of different cross sectional area. Direct

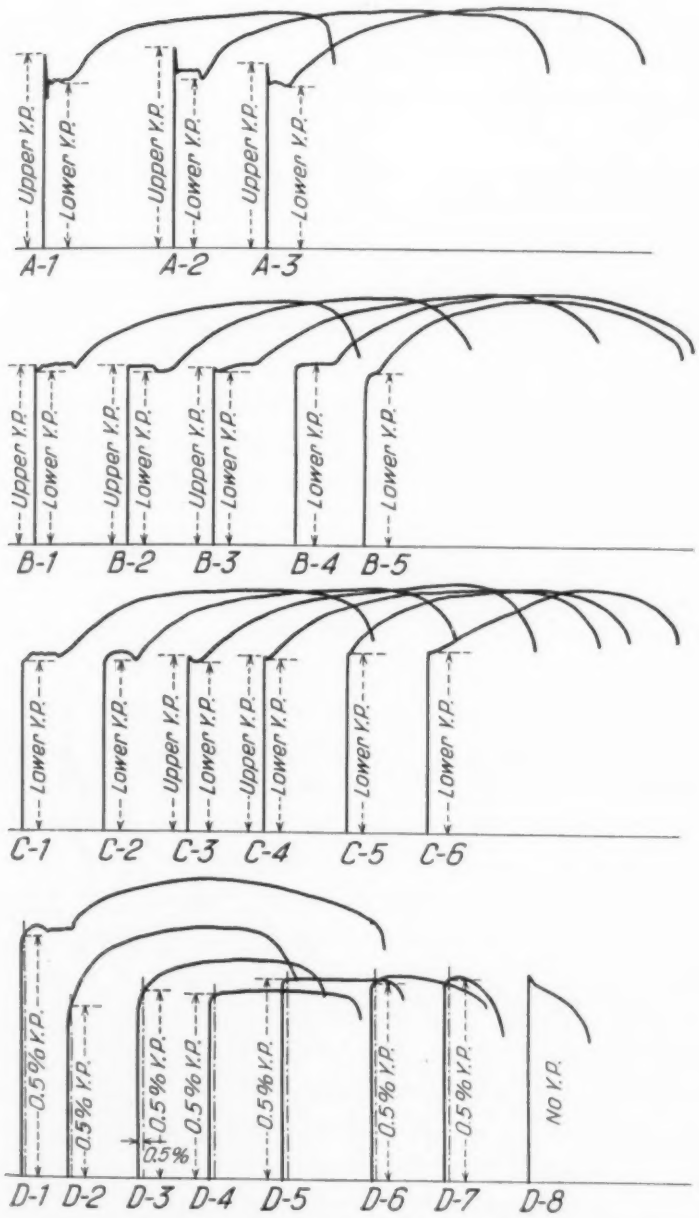


Fig. 7—A Group of Stress-Strain Curves Showing Variations in Upper and Lower Yield Point and in Yield Point Elongation.

comparisons can only be made of curves obtained from samples of the same cross section. The principal value of the stress-strain curve lies in the representation of the relationship between load and deformation rather than actual numerical values of the load. The yield point and tensile strength are computed in pounds per square inch from the load readings taken from the indicating dial of the

machine and it is not the purpose of the stress-strain curve to supply such values. Accurate curves can be used for checking back on the load readings, but this is of secondary importance.

There is considerable confusion in both verbal and written discussions of the tensile test in the proper use of the terms proportional limit, elastic limit, yield point, Johnson's limit, etc., and the reader is referred to standard text books on strength of materials, and in particular to the A.S.T.M. Tentative Standards, 1930, page 774 (E6-30T), for a complete discussion of these definitions. These different quantities are shown graphically in Fig. 6. The proportional limit and Johnson's limit require elaborate and accurate instruments for their determination, and it is only the yield point that is determined in commercial testing. Some materials will show a very sharp break in the curve corresponding to the yield point while others show a gradual transition from the elastic to the plastic state. When there is a definite yield point, it sometimes happens that the load drops quickly from the "upper" yield point to some lower value ("lower" yield point) at which most of the yielding takes place. Considerable work has been done on this by several German investigators, and it seems to be the censensus of their opinion that the "lower" yield point is characteristic of the material while the "upper" yield point depends upon testing conditions. Our own experience seems to bear this out, for samples cut side by side may show considerable variation in "upper" yield point, but will generally show good agreement in "lower" yield point. In any event the "lower" yield point is considered the more useful value. A study of Fig. 7 shows that there is considerable difference in the way this lower yield point occurs. For the sake of uniformity, it is necessary to agree upon the particular point to take. In this we have followed the rule given by Bach (4), who defines it as "the smallest value of stress to which the load sinks during stretching or the smallest load under which stretching proceeds." Bach has given examples of the application of this rule by marking upper and lower yield points on a number of curves in his published work. The typical curves shown in this paper have been selected from a large number actually drawn on our Amsler machine.

The upper yield point corresponds approximately to that determined by the drop of the beam in the lever type machines and since the A.S.T.M. and some other specifications define the yield point as the drop of the beam, the upper value is the one that should be

considered when the material is being tested to see if it will meet such specifications. In some cases, illustrated by curves B5, C2, C5, and C6, there is really no upper yield point and the value should be reported as lower yield point.

Cold-worked material shows a more or less indefinite yield point depending on the kind and amount of cold working. There is no logical method of defining it in such cases for, as a matter of fact, there is no yield point. It has proved useful, however, to set an arbitrary amount of strain for the location of the so-called yield point of such material. Various investigators have used different amounts varying from 0.1 to 1.0 per cent elongation. It is necessary to determine this graphically from the stress-strain curve and the scale of the curve therefore has to be considered. For the scale we have used the best value has been found to be 0.5 per cent elongation. This is easily measured from the curve with a special celluloid scale, the use of which will be described later. In some materials that have a very sharp yield point, there may be a sudden surge of the pendulum at the beginning of yielding and a corresponding fall in the load to an abnormally low value followed by a rise to some higher value which is more or less constant throughout the yielding. In such cases the momentarily low value should not be taken as the yield, but rather the rule to follow is that there must be a definite deformation.

From this discussion it will be seen that the following types of yield points have been distinguished:

Upper Yield Point is that stress at which yielding begins.

Lower Yield Point is the smallest value of the stress to which the load sinks during stretching or the smallest load under which stretching proceeds.

0.5 Per Cent Yield Point is the stress corresponding to an elongation of 0.5 per cent of the gage length as determined from the stress-strain curve.

The percentage elongation generally referred to in connection with tensile tests is the per cent elongation after fracture; this is the "total" elongation. There are two other elongation values that are considered significant, the "yield point elongation" and the "uniform elongation." The first mentioned is the per cent elongation which is necessary to pull the sample entirely through

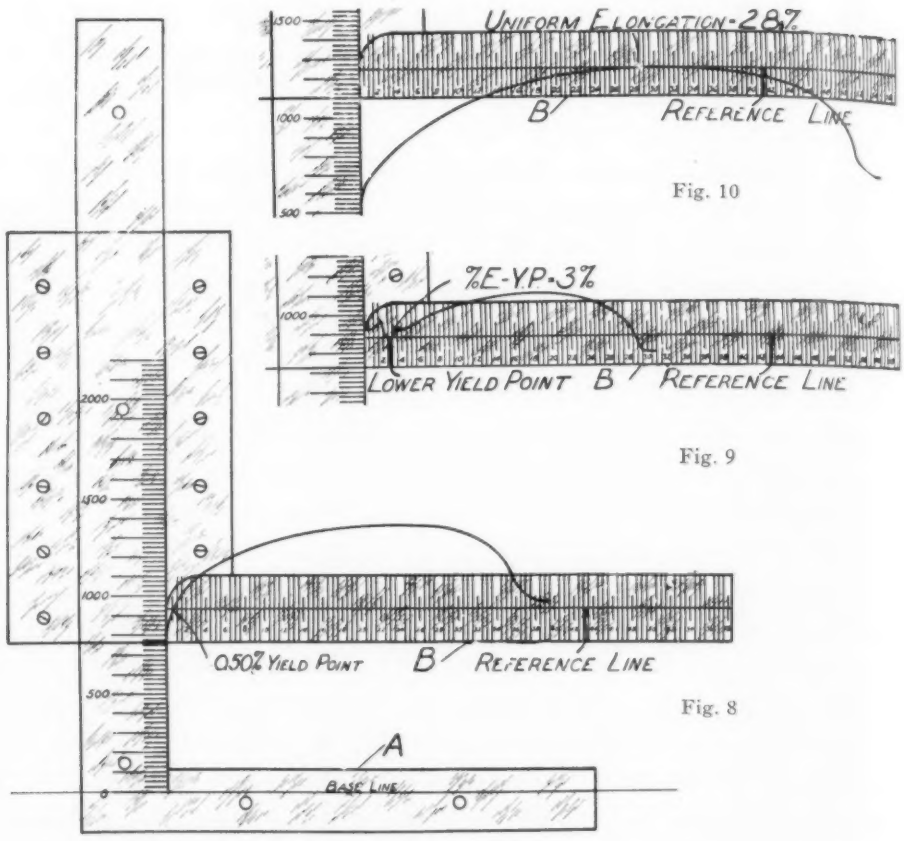


Fig. 10

Fig. 9

Fig. 8

Fig. 8—Special Scale for Measuring the Stress-Strain Curves Showing the Scale in Position for Measuring the 0.5 Per Cent Yield Point, which in this Case is 935 Pounds.
Fig. 9—Inset Showing Determination of Yield Point Elongation of 3 Per Cent.
Fig. 10—Inset Showing How Uniform Elongation is Measured. In This Case 28 Per Cent.

the yield point and this, of course, can only be determined on material which has a sharp yield point and, furthermore, it is necessary to take this value from the stress-strain curve. The uniform elongation is the amount of stretch which the sample undergoes up to the instant that local contraction starts. It has been shown (6) that up to this instant the elongation is uniform over the entire gage length. The elongation corresponding to this value can best be determined from the load-deformation curve (10).

Special Scale for Measuring Stress-Strain Curves

In order to make these graphical measurements of yield point elongation and uniform elongation, a special celluloid scale has been designed and the use of this is shown in Figs. 8, 9, and 10.

It consists of two parts, the stationary arm A, and the movable arm, B. To use it, the base line on the horizontal part of A is placed directly on the base line of the curve to be measured, at the same time lining up the right side of the vertical scale on the origin of the curve. The movable arm, B, can now be moved up or down until the scale overlaps the yield point of the curve. If this is not sharp, the 0.5 per cent line on the scale will give the proper point for the 0.5 per cent yield point (see Fig. 8). The fine line down the middle of scale B is the reference line and the arm is moved until the

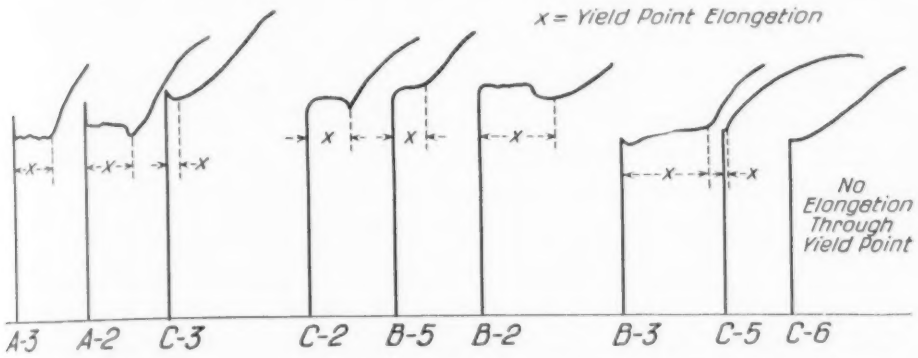


Fig. 10a—Measurement of Yield Point Elongation. Arrows Indicate Amount of Elongation.

0.5 per cent division mark and this reference line intersect on the curve (without moving A). The reference line is then followed to the left to the vertical scale and the yield point value read off in pounds.

If the material has a definite yield point, the value of the load taken for it is not determined graphically as just described, although a value so determined will generally agree quite closely with the dial reading. To determine the yield point elongation on specimens showing a definite yield, the horizontal scale on B is moved until the reference line and the graduations line up with the point at which the curve begins to rise again after passing through the yield point. The corresponding per cent elongation is recorded as the yield point elongation. This scale on B is marked to read directly in per cent elongation on a 2-inch gage length when the elongation is magnified 10 times. Fig. 9 shows the use of the scale for making this determination.

Fig. 10a shows the yield point elongation on several types of curves. The general rule is to consider this complete at the point where the curve starts upward the last time.

The stress-strain curve usually has a portion at the top which is perfectly flat for a short distance. This is where the increase in unit strength due to cold-working is exactly offset by the decrease in section due to local necking. The *initial* point of this flattening is the one that determines the uniform elongation. The arm B (Fig. 10) is moved until the reference line is tangent to the flat portion of the curve. The elongation corresponding to the point farthest to the left at which the line and the curve coincide is read from the scale on B. In order to check the accuracy of the extensometer readings and of the curve, it is advisable to measure the total elongation from the curve as well as from the sample.

The elastic ratio, yield point divided by tensile strength, is a useful quality factor of sheet material. The yield point value to be taken for this should be the lower value when the material exhibits one, otherwise the 0.5 per cent value.

Interpretation of Stress-Strain Curves

The interpretation of the stress-strain curve may be made from: first, the numerical values taken from it, and second, its shape. Of the numerical values that can be obtained only from the full-drawn stress-strain curve, the yield point elongation and uniform elongation are the most important. The significant features of the shape of the curves are: presence or absence of a sharp yield point, radius of curvature at transition from the elastic to the plastic state, amount of elongation through the yield point, amount of uniform elongation, elastic ratio, elongation from maximum load to breaking point, and total elongation.

The measurement of the yield point elongation has been described. This quantity may vary from zero up to as much as 10 per cent according to the treatment the material has received. The importance of this measurement lies in its ability to indicate the intensity of stretcher-straining. It has been known for some time that material with a sharp yield point will stretcher-strain and material without a sharp yield point will not (1), (11), and (12), but so far as we know there has been no demonstration of a quantitative relationship between these two phenomena. This we propose to furnish.

Experience has shown that of two materials with the same yield point elongation, the one with the smoother surface will stretcher-strain the more, and it is therefore necessary to assume for purposes

of discussion that the material is of a uniform degree of smoothness. If a test specimen of soft-annealed high-finish mild steel is observed during the early stages of the tensile test, it will be seen that the stretcher strains begin to form the instant the yield point is reached and that they extend until they have covered the entire parallel section of the specimen. The instant that the entire parallel section is covered, or rather the instant that all the strains have "pulled-out," the load will begin to rise again out of the yield point portion of the stress-strain curve. This suggests that the greater the depth of the stretcher strains the greater the yield point elongation will be. This is reasonable since the deeper the stretcher strains the greater the elongation corresponding to that amount of reduction of area and the more the material must be stretched in order to pull out all of the strains and restore an approximately smooth surface and uniform cross section. When the specimen has reached the end of the yield point elongation, it is approximately true and may be assumed for purposes of computation, that the entire gage length has been reduced in thickness by an amount equal to the depth of the deepest stretcher strain. The reduction in thickness and the yield point elongation are therefore related and either can be computed from the other on the assumption that the gage length portion of the specimen remains a prism and that the volume is constant.

If A_o and L_o are the original cross section and length, respectively and A_1 and L_1, the corresponding values at the end of the yield point elongation, then

The Yield Point Elongation per inch

$$= \frac{L_1 - L_o}{L_o} = \frac{L_1}{L_o} - 1 \qquad (1)$$

Assuming that the sample remains a prism,

$$A_o L_o = A_1 L_1 \qquad (2)$$

and,

$$\frac{L_1}{L_o} = \frac{A_o}{A_1} \qquad (3)$$

Subtracting 1 from each side of this equation,

$$\frac{L_1}{L_o} - 1 = \frac{A_o}{A_1} - 1 \qquad (4)$$

or,

the yield point elongation per inch

$$= e_{y.p.} = \frac{A_o}{A_1} - 1 \qquad (5)$$

Letting t_o, w_o, t_1, and w_1 represent the original and final thicknesses and widths,

$$A_1 = t_1 w_1 \qquad \text{and} \qquad A_o = t_o w_o \qquad (6)$$

If the thickness and width may be considered to change relatively the same amount,

$$\frac{w_1}{t_1} = \frac{w_o}{t_o} \qquad \text{and} \qquad w_1 = \frac{w_o}{t_o} t_1 \qquad (7)$$

Substituting in (5) we have,

$$e_{y.p.} = \left[\frac{t_o}{t_1} \right]^2 - 1 \qquad (8)$$

Since the change in thickness, $\triangle t = t_1 - t_o$, we can solve (8) for t_1, and then substitute $\triangle t + t_o$ for t_1 and solve for $\triangle t$ with the following result,

$$\triangle t = t_o \left[\frac{1}{\sqrt{e_{y.p.} + 1}} - 1 \right] \qquad (9)$$

In this equation $\triangle t$ is theoretically equal to the sum of the depths of the stretcher strains on both sides of the sheet. This result has been obtained on the assumption that both the width and the thickness decrease in the same proportion, i.e., if the thickness decreases one per cent, the width will do likewise. This probably holds for only relatively small values of w/t, such as for tensile test specimens. On large drawn parts the proportional change in the width is likely much less than proportional to the change in thickness, and the yield point elongation in such a case is nearly all accounted for by reduction in thickness. If the width is considered to remain constant and the thickness to decrease in proportion to the elongation through the yield point, another relationship holds between these quantities. This is expressed by the equation:

$$\triangle t = t_o \left[\frac{1}{e_{y.p.} + 1} - 1 \right] \qquad (10)$$

Equations (9) and (10) represent extreme limiting conditions of the w/t relationship. It is important to note that the value $e_{y.p.}$ in equation (10) must be determined on the wide piece which has been assumed to suffer no change in width during the yield point elongation. This leads to the now obvious conclusion that the $e_{y.p.}$ value in equation (9) will be greater than that in (10) due to the fact

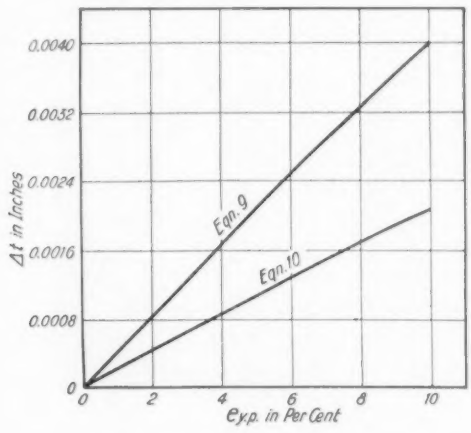


Fig. 11—Relationship Between Yield Point Elongation and Depth of Stretcher Strains.

that on the narrower piece the elongation is due to decrease in both width and thickness. The relationship between $\triangle t$ and $e_{y.p.}$ is shown in Fig. 11 according to both equations for sheet of 0.044-inch thickness. The value $e_{y.p.}$ is different for the two equations, i.e., if a regular test piece is used to determine $e_{y.p.}$, this value cannot be used in equation (10).

Actual tests confirm the relationship between yield point elongation and severity of stretcher straining. Fig. 12 shows five stress-strain curves which have different amounts of elongation at the yield point. A duplicate sample was cut adjacent to each of the specimens from which the curves were made and these were pulled in the testing machine one-half the amount of the yield point elongation of the companion samples. The surface appearance of these pieces is shown. The yield point elongations measured from the five curves are as follows: (A) 9.0 per cent, (B) 3.5 per cent, (C) 1.6 per cent, (D) 1.0 per cent, (E) 0 per cent. It will be seen that the stretcher strains are most severe on (A) and least noticeable on (D), while (E) is entirely free from them.

A study of the minute details of the stress-strain curves reveals

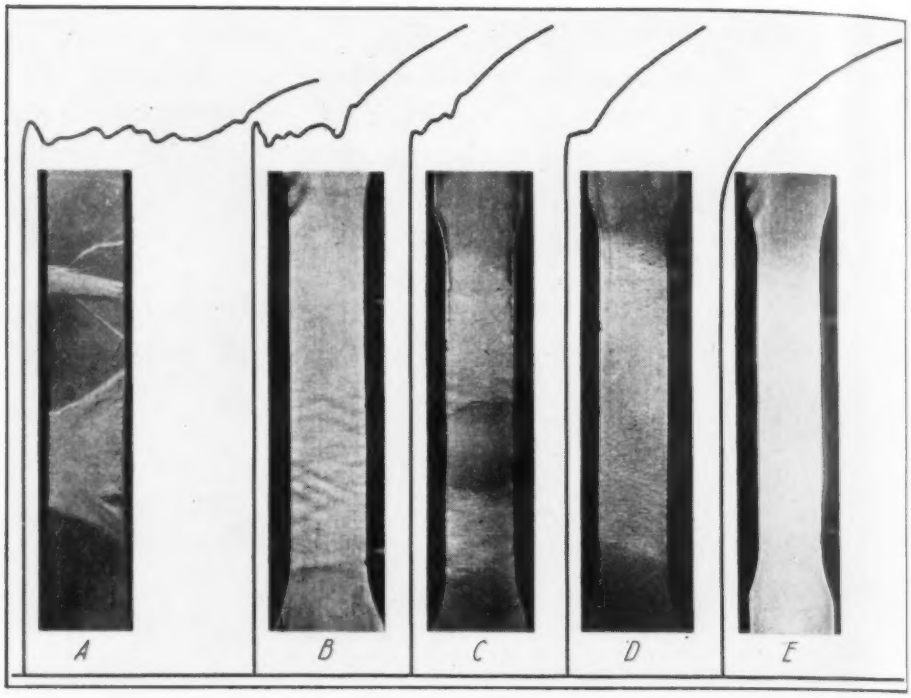


Fig. 12—Five Stress-Strain Curves which Have Different Amounts of Elongation at the Yield Point. The Surface Appearance of the Test Piece is also Shown for Each Curve. The Yield Point Elongation Measurements from the 5 Curves are as Follows: A—9 Per Cent; B—3.5 Per Cent; C—1.6 Per Cent; D—1.0 Per Cent; and E—0 Per Cent.

how faithfully they record the behavior of the metal during the test. When numerous fluctuations occur at the yield point, it is found that these are coincident with the formation of the individual stretcher strains or groups of them. In some cases the stretcher strains that form at the ends of the parallel section due to stress concentration at the shoulders, progress uniformly toward the center of the gage length. In this case the curve is fairly smooth through the yield point, but shows a dip before the load rises again (see Fig. 13). This final dip occurs when the two stretcher strains or sets of stretcher strains meet or overlap.

When the first stretcher strains occur entirely outside of the gage length, there is no corresponding elongation recorded on the curve, but the drop in load is registered and produces the result shown in Fig. 14 at point (A). An inaccurate extensometer will frequently produce curves having this characteristic, but even an accurate one will occasionally give this kind of a result from the cause just mentioned.

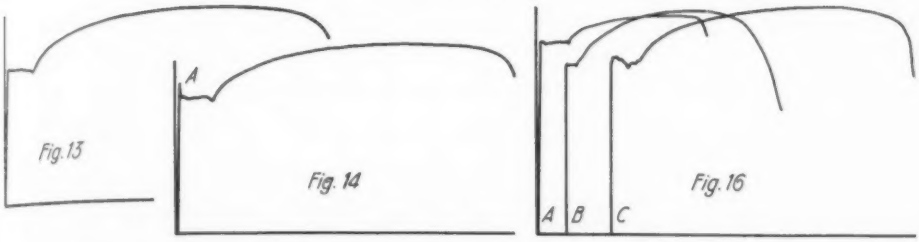


Fig. 13—Stress-Strain Curve Which Has a Dip at the End of the Yield Point Elongation Due to the Meeting of Two Sets of Stretcher Strains.

Fig. 14—Stress-Strain Curve When First Stretcher Strain Occurs Entirely Outside of the Gage Length.

Fig. 16—Curve A Shows Practically no Elongation from Maximum Point to Fracture Point; Curve C Shows Long Flat Portion at Maximum and Considerable Elongation from this Point to Fracture; Curve B Shows Less Elongation from Maximum Point to Curve but Breaking Load is Much Less Due to Tearing of Sample.

In the case of most stampings it is desirable that the metal thickness never decrease below a certain minimum value. This requirement is based on both the physical strength and the surface appearance. The capacity of the material to withstand severe draws without local reduction is measured by the uniform elongation.

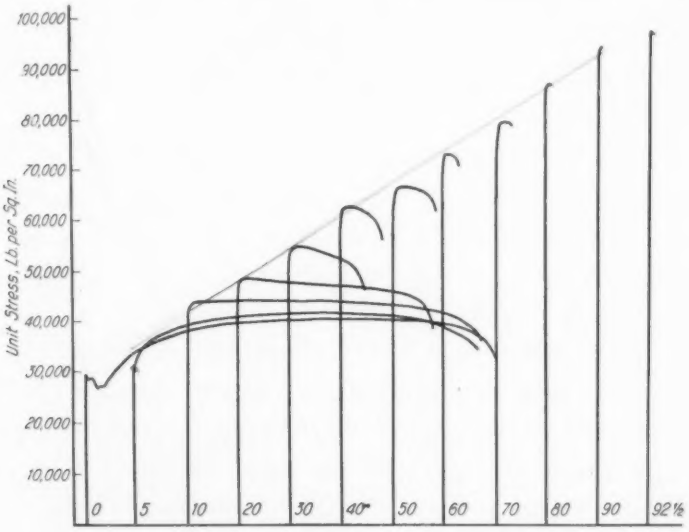


Fig. 15—Stress-Strain Diagram for Cold-Rolled Material Ranging from No Cold Work to 92.5 Per Cent. The Higher the Amount of Cold Rolling the Sharper is the Radius of Curvature at the Transition from the Elastic to the Plastic State.

From the general appearance of the stress-strain curve a number of significant characteristics of the material may be recognized. Soft annealed mild steel shows a sharp yield point which disappears if the material is given a sufficient amount of cold rolling. The amount required varies somewhat from one lot of steel to another. With higher

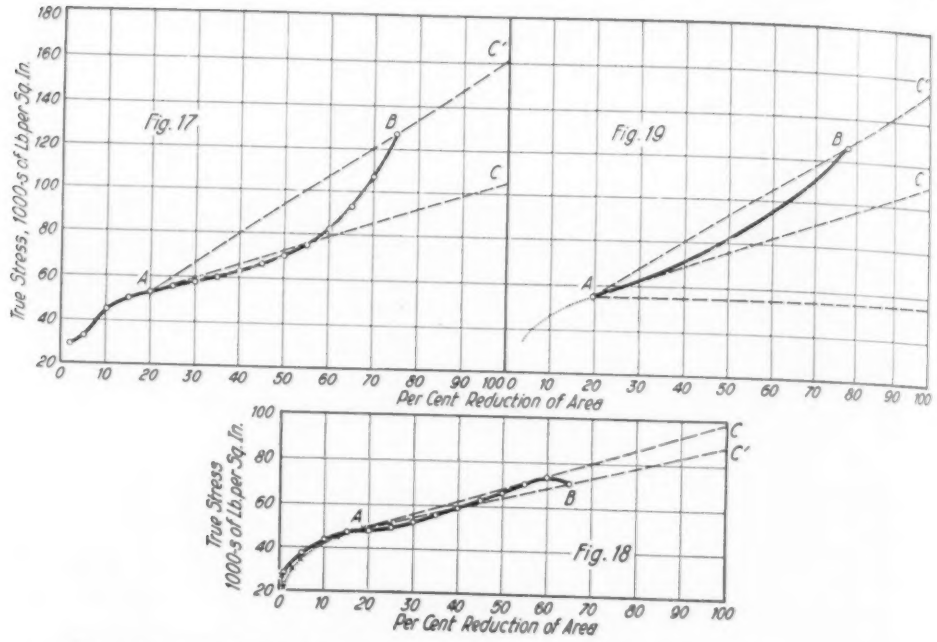


Fig. 17—True Stress Curve for Armco Iron. 0.505 Inch Round Specimen. Plotted from Diameter Measurements made During the Course of the Test.
Fig. 18—True Stress Curve for a 19 Gage Armco Iron Sheet. Plotted from Cross Section Measurements made During the Course of the Test.
Fig. 19—True Stress Curve for an 18 Gage Armco Iron Sheet. Plotted from an Autographic Stress-Strain Diagram by Computing Reductions from Elongation. (Up to Uniform Elongation.)

amounts of cold rolling the radius of curvature at the transition from the elastic to the plastic state is a rough indication of the amount of cold work the material has received. The higher the amount of cold rolling the sharper the curve at this point. This is shown in Fig. 15. When the autographic stress-strain curves are drawn with the equipment that has been described, the reduction in load beyond the "maximum" is faithfully recorded even to the point of fracture. This makes it possible to determine the breaking load, which is of some value in plotting the "true-stress" curves to be described presently. The appearance of the curve from the maximum load to the breaking point gives some idea of the reduction of area at fracture although this is only relative. For example, curve (A) in Fig. 16 shows little elongation from the maximum point to fracture and the sample actually had practically no reduction of area. Curve (C) shows a long flat portion at the maximum and considerable elongation from this point to fracture. This sample had about seventy per cent reduction of area at fracture. Curve (B) has less elongation from the maximum load to the break than

(C), but the breaking load is much less. This is sometimes the result of a tearing action at the fracture which causes one side of the specimen to rupture before the other and the load is gradually released before the sample is entirely broken or, rather, torn in two. The sloping line down to the breaking point is an indication of this behavior. The characteristics of the curves just described cannot be used to give more than a rough indication of the reduction of area, but the point is worth remembering when examining curves for material of widely different properties.

True-Stress Curves

In the ordinary tensile test, the stress is always computed on the basis of the original area, but for certain theoretical reasons it sometimes is desirable to determine the true stress, which is based on the minimum cross sectional area. Methods for constructing these true-stress curves can be found elsewhere (9), but it may be said briefly that they consist in measuring the minimum cross sectional area of the specimen during the test. To do this it is necessary to use a specimen which lends itself to such measurements. Obviously a round piece is better than a flat sheet specimen and for this reason it is more difficult to prepare true-stress curves for sheet material than for round bars. When round bars are used and actual measurements are made in the manner mentioned, the resultant curve has the appearance of Fig. 17 which is a test on a 0.505-inch round bar of Armco ingot iron. Point A corresponds to the end of uniform elongation where necking begins; point B is the breaking point. All values of reduction of area up to Point A can be computed from the elongation, on the assumptions that were made in computing depth of stretcher strains from yield point elongation. Using the same notation as in equations (1) and (2) and letting q equal the per cent reduction of area, and e the per cent elongation, we have,

$$A_o L_o = A_1 L_1 = A_o (1-q) \quad . \quad L_o (1+e) \tag{11}$$

$$e = \frac{q}{1 - q} \tag{12}$$

$$\text{and } q = \frac{e}{1 + e} \tag{13}$$

This enables us to plot a true-stress curve from the stress-strain curve up to the point where necking starts and this much can therefore be easily done on sheet samples. The point on the true-stress curve which is considered to be of greatest significance, however, is C (Fig. 17), where the curve should theoretically meet the 100 per cent reduction of area line. Of course such a high reduction of area is never attained, but the true stress corresponding to this point is called the "extreme stress" and is considered by some to be an indication of the total inherent strength of the material if it could be completely utilized. Theoretically this "extreme stress" should be exactly twice the true stress at A and furthermore the tangent to the curve at A should pass through C. The angle a which this line makes with the horizontal axis is a measure of the rate of strain hardening. The steeper this line the more the material hardens up with a given amount of cold working.

Extended theoretical discussions of these true-stress curves can be found (9), but these are almost exclusively confined to results on round bars. Crane (8) has applied the theoretical analysis of such curves to the deep-drawing problem, but in the absence of published data on true-stress curves for sheet specimens has, of necessity, been forced to base his studies on the assumption that true-stress curves for sheets will resemble those on round bars. The principal difficulty in obtaining these curves on sheets is the accurate measurement of the cross section during the test. Sachs (9) has given an approximate method of determining the slope of the line AC (Fig. 17) by computing only two points: the true-stress at the point where necking starts and the true-stress at fracture. There is considerable evidence, however, to show that point B is nearly always above the line AC and it can be seen from Fig. 17 that if the slope of AC were determined by point B that C would fall much higher (at C^1). This is the weak point in this method and yet it is about the only one that can be used if the cross section cannot be measured during the test.

Another question that arises in the use of true-stress curves is whether the slope of AC or AC^1 is the proper measure of rate of work hardening. In some cases there is quite a difference in the two values. As a matter of fact neither line actually represents the behavior of the material; only the curve, which must be plotted from data obtained from actual measurements, portrays the real rate of hardening. For these reasons it would seem that the approximate

methods that have been suggested for obtaining true-stress curves and measurement of rate of strain hardening are subject to such large errors that their value is questionable. Two other true-stress curves for sheet samples are shown in Figs. 18 and 19 and illustrate the difficulties mentioned. Fig. 18 was drawn from instantaneous load, elongation, and cross section measurements made during the testing of a specimen of 19 gage Armco ingot iron sheet. The relation between the extreme stress values obtained by the two methods is seen to be reversed in the case of Fig. 18. The solid line is plotted from the reduction of area measurements while the dotted line up to the point A is from reductions computed from the measured elongations. In Fig. 19 the autographic stress-strain curve of an 18-gage Armco ingot iron sheet furnished the elongations up to the maximum load which were converted into reduction of area values by the use of equation (13). The true stress at fracture was then computed and line AB drawn and extended to C^1. Point C is located at a true stress twice that at A. The same remarks apply to this curve as were made in connection with Fig. 17. The only thing that the accurate autographic stress-strain curve has contributed to this study is greater ease in constructing curves like Fig. 19. From it the uniform elongation can be readily determined and, if desired, the breaking load also, so that point B can be located. The latter is unnecessary, however, if the slope of the work hardening line is taken tangent to the curve at A. In this case it is not even necessary to plot the curve since the relationships can be determined analytically.

If A_o is the original cross section
L_u is the maximum load
e_u is the uniform elongation
q_u is the reduction of area at the uniform elongation
S_u is the true stress at the uniform elongation
S_x is the true stress at 100 per cent reduction of area
$\tan \alpha$ is the slope of line AC (Fig. 19)

Then,

$$\tan\alpha = \frac{S_x - S_u}{1 - q_u} = \frac{S_u}{1 - q_u} \qquad (14)$$

but since

$$S_u = \frac{L_u}{A_o\ (1-q_u)} \quad \text{and} \quad q_u = \frac{e_u}{1 + e_u} \qquad (15)$$

we have

$$\tan\alpha = \frac{L_u\ (1 + e_u)^2}{A_o} = (\text{Tensile Strength})\ .\ (1+e_u)^2 \qquad (16)$$

The determination of the uniform elongation from the accurate stress-strain curve, therefore, considerably reduces the amount of work in computing tan α. The interpretation of the values so obtained must rest upon the results of further work.[5]

Summary

It has been shown that special equipment and technique are necessary in order to obtain accurate stress-strain curves for the tensile test. Both have been described and examples presented to indicate the various types of curves obtained on mild steel deep-drawing sheets. The significant characteristics of the curves have been discussed and a special scale described for measuring certain features. Experimental results confirm the previously stated theory that stretcher strains and a sharp yield point are related and show that the greater the amount of elongation at the yield point the more severe the stretcher straining. Increasing amounts of cold rolling cause a decrease in the radius of curvature at the transition from the elastic to the plastic portion of the curve. By means of the data obtained from accurate stress-strain curves, it is possible to construct the true-stress curves for sheet tensile samples, but it is brought out in the discussion of several of these curves that the measures of rate of strain hardening as well as "extreme stress" obtained from them are subject to large errors which makes them of questionable value.

Acknowledgments

The special extensometers and curve-measuring scales were constructed by J. C. Young, to whom much credit is due for his

[5]It can be shown that Sachs' approximate method of constructing the true-stress curve and the value of tanα obtained from it can be arrived at analytically in a manner similar to that shown above. The resulting equation is:

$$\tan\alpha = \frac{\frac{L_b}{A_b} - \frac{L_u}{A_u}}{\frac{A_b}{A_o} - \frac{A_u}{A_o}}$$

where L_b and A_b are breaking load and area of fracture respectively, and A_u is the area at the end of uniform elongation.

helpful suggestions. The authors also wish to express their appreciation to R. O. Griffis and to Robert F. Mehl for their helpful criticisms and pertinent suggestions.

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DISCUSSION

Written Discussion: By Dr. Ing. A. Nadai, Research Laboratories, Westinghouse Electric and Mfg. Co., East Pittsburgh.

The paper by Messrs. R. L. Kenyon and R. S. Burns is a further valuable contribution to the interesting subject of the phenomena occurring in soft steel when the limit of plasticity is reached; phenomena, which, as the authors mention in their paper, have attracted the attention of various investigators more recently, particularly in Germany and in England. Although some of the first observations with reference to the drop of the yield stress of mild steel are known 25-30 years and since perhaps C. Bach has probably first called attention to the existence of the upper and lower yield points of steel, various other

important details connected with the drop of the stress at the upper yield point of mild steel have been the subject of investigations more recently. It is particularly worthwhile to mention here perhaps the influence of the shape of the test piece in a tensile test on the drop of stress, the effect of temperature or of heat treatment besides cold work and the effects of small stress concentrations (presence of small notches or holes) on the appearance of strain figures in plastic materials, questions which have been treated more recently in connection with the subject.

Aging seems to have a deep effect on producing high upper yield points, as has been shown by P. Ludwik and Scheu (*Stahl und Eisen*, 1925), who could raise the upper yield point of certain prestressed and subsequently slightly heated iron or steel specimens even above the ultimate strength. It is furthermore known that when a material has a well defined or sharp yield point (sharp limit of plasticity) in the tensile test, this leads to an instability of the static equilibrium, the result of which is the formation of a comparatively thin layer in which the plastic deformation is first localized (slip or flow layer). At the Westinghouse Research Laboratories we became particularly interested in these things and have investigated them from various sides, also in connection with previous observations by W. Köster,[1] according to which the nitrogen content in steel is the cause of the darkening of the plastically deformed layers by Fry's etching method. This has been verified by Messrs. C. W. MacGregor and F. R. Hensel in a paper recently published.[2]

The authors describe the figures, which appear on the surface of a mild steel specimen, particularly if it has been well polished, just when the yield point has been reached. They call these figures "stretcher straining figures". A closer observation of similar figures produced also under more complicated distributions of stress has brought out many interesting details about the mechanism in which plastic materials start to yield. To the writer of these lines they have been of particular interest for many years mainly for the reason that they can be utilized as a means to make visible the distributions of stress while materials are in the plastic state, as has been described by the writer at various occasions. In England these figures are called strain or flow figures, in Germany they are known as flow figures (Fliessfiguren) or slip lines (Gleitlinien), where a thin layer of the plastically deformed material intersects the surface of the specimen; while in this country they seem to be known as "Lüder's lines". It seems to the writer that no particular reason may be advanced to introduce the name "stretcher straining", for the same thing and this less used name should rather be omitted when dealing with strain figures or Lüder's lines.

It is perhaps worthwhile to mention finally, at least with a word, another means which serves also to make visible flow figures. This is a slight concentration of stress produced in a (polycrystalline) material having a sharp yield point, such as mild steel at normal temperature. By means of small notches

[1] "Das Wesender Aetzfiguren," *Arch. Eisenhuettenwesen*, Vol. 3, p. 637-658, 1930, cf. also other papers by Köster.

[2] "The Influence of Nitrogen in Mild Steel on the Ability of Developing Flow Layers," *Journal of Rheology*, Vol. 3, No. 1, January, 1932.

or holes, distinct slip layers can be produced on a well polished specimen of such materials. These effects have been described elsewhere by the writer and his collaborator, so that further points need not be discussed here in detail.

Written Discussion: By C. W. MacGregor, Research Laboratories, Westinghouse Electric and Mfg. Co., East Pittsburgh.

It is pleasing to note that more attention is now being paid in this country to the phenomenon of the upper and lower yield points as exhibited by mild steel. Until recently many engineers considered only the upper yield point in their specifications of materials. This is probably due partly to the fact that the beam type testing machine was formerly used in the great majority of laboratories to the exclusion of the hydraulic type machine which has a continuous equilibrium of its force-indicating device. The latter type machine provides an easier determination of the lower yield point. The writer is also

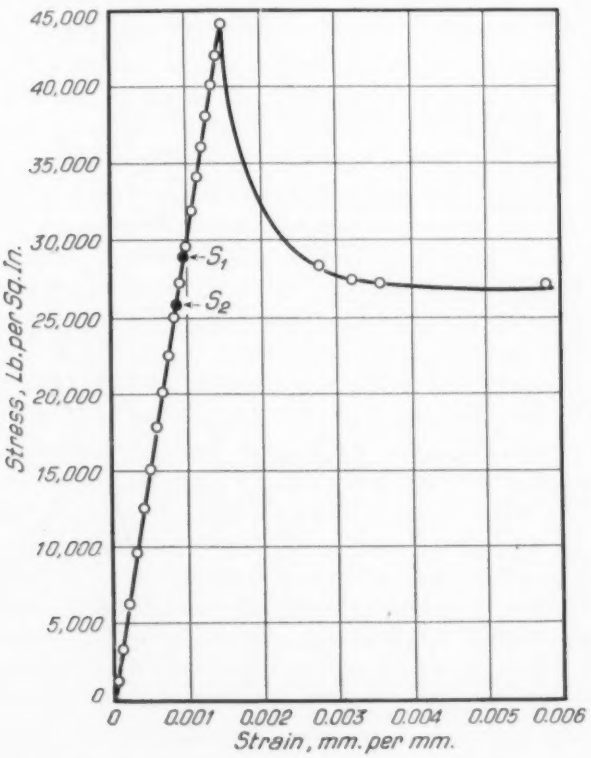


Fig. 1—Portion of Stress-Strain Curve for Round Tensile Test Bar.

glad to learn that the experiences of the authors of this paper seem to further emphasize that the lower yield stress is the more reliable of the two yield values. The upper yield stress has been shown to be affected by many different testing conditions.

The autographic device described by the authors is no doubt a distinct improvement over the older types. It will be especially valuable for routine testing in which too much time would be otherwise required in using an extensometer of some sort. The older types were mainly of value in giving a

qualitative picture of the course of deformation. It is advantageous to have a continuous diagram of the test, especially now that more attention is being paid to certain portions of the diagrams which until recently were usually neglected, such as the yield point extension, uniform extension, etc.

The drop in load at the yield point for flat test bars such as those used in the present paper is usually not as pronounced as that obtained in round bars of the same material. This has been pointed out by Bach[3] in some of his early tests. The stress distribution over the cross section of a round bar is more uniform than that in a flat bar and consequently a higher yield stress will be obtained. A further reason is that a flat bar is always more difficult to center in the testing grips than a round test piece, and consequently there is often some bending introduced, which prevents the attainment of a high yield stress. When various precautions are observed concerning testing procedure and design of test pieces, extremely large differences between upper and lower yield points may be obtained. Fig. 1 (this discussion) shows a portion of a stress-strain diagram recorded by means of a Martens extensometer on a round bar suitably designed containing large fillets near the heads so as to reduce stress concentration. Readings were taken through a portion of the lower yield point. It is seen that a difference of 38.5 per cent between the upper and lower yield points in per cent of the upper is obtained in this case.

A further point of interest which may be mentioned is illustrated by Fig. 12 of the paper. It is here quite clearly shown that the sharper the transition from the elastic to the plastic state, the more pronounced will be the flow layers received; a conclusion which also confirms the experiments made by the writer some time ago on various mild steels.

Written Discussion: By Joseph Winlock, chief metallurgist, Edw. G. Budd Mfg. Co., Philadelphia.

I have read with a great deal of pleasure and profit this excellent paper by Messrs. Kenyon and Burns. They have clearly shown the importance of the stress-strain diagram in studying some of the phenomena which take place in the deep drawing of sheet and strip steel. Their novel and ingenious method of obtaining these diagrams and their thoughtful attention to details in their description of it will be of great assistance to those interested in this subject. In my opinion, this paper marks a significant step forward in our progress toward acquiring a greater knowledge of the properties of sheet and strip steel for deep drawing purposes.

I hope these authors will continue their research work in this field and will study the effect of certain physical characteristics of sheet and strip steel, such as grain size, carbon content, preferred orientation of the crystalline grains induced by cold rolling, etc., upon the stress-strain diagrams which they are now able to obtain.

I should like to congratulate the authors for their constructive paper and I am looking forward with pleasure to any future papers by them on this interesting subject.

Written Discussion: By Edward V. Crane, staff engineer, E. W. Bliss Co., Brooklyn, N. Y.

[3]C. V. Bach, Z. V. D. I., Vol. 49, 1905, I, 615; Mitt. Forschungsergebnisse Heft, Vol. 29, 1905, I, 61.

The authors' discussion of equipment and of stretcher strains in sheet metal should prove a real contribution to gradually expanding knowledge of plastic working of metals.

Unfortunately the writer is unfamiliar with the work of Sachs. In Figs. 17 and 18 we can find no practical significance for the points A, B, C and C_1 or justification for a 2 to 1 relation between points A and C.

These two figures do offer a most interesting comparison of true stresses, testing in one case a round bar and in the other a sheet specimen. A number of points of similarity and difference are apparent. Using large scale plottings of the two curves, an extension of the straight line sections gives a rate or modulus of strain-hardening $S_x/1.00$, of 93,000 and 99,000 respectively. The difference is not great and, with some allowance for the human factor in taking the measurements, is probably due to some small difference in carbon or manganese content.

In the accompanying Fig. 2 the writer has replotted both curves to a common strain-hardening line. Note that at about the same point, around

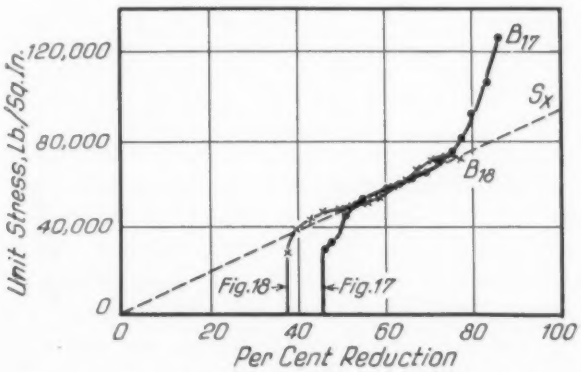


Fig. 2—True Stress Curves for Armco Iron Sheet and Rod Translated Relative to Their Modulus of Strain-Hardening.

70 per cent absolute reduction, all of the (most?) favorably oriented slip planes have been used up and the stress starts to climb more rapidly as the curves depart from the straight line. In the case of the strip sample a fracture begins to develop almost at once and the stress drops off until the failure is complete. The curve for the round sample continues to rise more and more rapidly to ultimate failure. If the work had been squeezing, rolling or wire drawing it might have gone even farther, especially with the aid of generated heat; and failure would probably have developed internally.

The form of chart shown in Figs. 2 and 3 has been adapted to bring out the uniformity of the strain-hardening or cold-working process regardless of extent of annealing or subsequent plastic working. In practice the junction of the elastic and plastic curves, Fig. 2, takes a variety of shapes, depending perhaps upon relative direction of previous working. In Fig. 3 the elastic lines for Figs. 17 and 18 of the paper have been continued to a theoretical yield point at their junction with the plastic curve.

From the theoretical yield points and the relative positions of the test

curves on the strain-hardening line it will be noted that the sheet sample, Fig. 18 of the paper, was annealed to a softer and more plastic state than the bar sample, Fig. 17. Therefore the plastic range (between the theoretical initial yield point at the low limit and the point at which favorably oriented slip planes have been used up and the curves begin to rise sharply as the high limit) is greater for Fig. 18 of the paper (S_1 to S_4 = 59 per cent reduction)

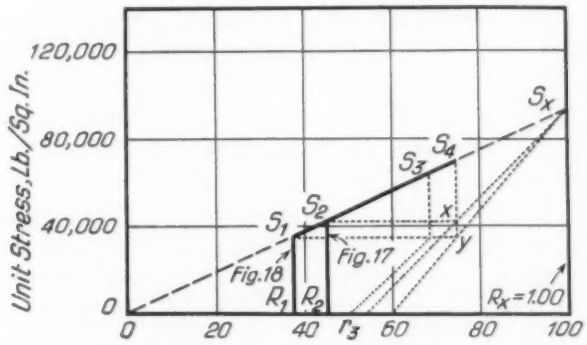


Fig. 3—Theoretical Curves and Diagrammatic Relations of the True Stress Curves Shown in Figs. 17, 18 and 20 of the Original Paper.

than for Fig. 17 (S_2 to S_4 = 54 per cent reduction). This plastic range is a measure of the cold-working which can safely be performed upon a metal without reannealing.

The theoretical initial yield point (S_1 and S_2) can be computed from a true stress curve regardless of eccentricities of the test yield point, provided the modulus of strain-hardening (S_x) for the particular analysis is known. Constant temperature should also be assumed as we believe that the rate of strain-hardening is less with higher temperatures. It will be noted in Figs. 17, 18 and 19 of the paper that a test value of 30 per cent reduction (r) falls in each case upon the straight portion of the test curve and therefore upon the strain-hardening line. From this the initial yield point S_1 (or S_1 Fig. 18 or S_2 Fig. 17 in Fig. 3) can be computed from:

$$S_1 = \frac{S_r - r\ S_x}{(1 - r)} \qquad (1)$$

or for r = 30 per cent

$$S_1 = \frac{S_{30} - .30\ S_x}{(1.0 - 0.30)} \qquad (2)$$

and the corresponding absolute reduction (R) will be

$$R_1 = \frac{S_1}{S_x} \qquad (3)$$

Methods of arriving at various relative values diagrammatically are shown in Fig. 3 of this discussion. These may all be expressed in simple formulæ. Thus the working or test reduction (r) which is possible from an initial yield point

S_i to a given upper limit S_u (or S_4 in Fig. 3) is:

$$r = \frac{S_u - S_i}{S_x - S_i} \qquad (4)$$

or for curve 17 $\quad r = \dfrac{S_4 - S_2}{S_x - S_2}$ (= approx. 54%, see line S_x, X, 54)

The maximum or final stress for a given reduction (in thickness, crosssection area, or shell diameter) is:

$$S_m = S_i + r_m (S_x - S_i) \qquad (5)$$

or for curve 18 and a reduction $r_n = 50\%$ or 0.50;

$S_3 = S_i + 0.50 (S_x - S_i)$ (see construction, using radial line from S_x to 50 per cent).

In all of these formulæ:

S_x = Modulus of strain-hardening in pounds per square inch.
S_i = Actual unit stress at theoretical initial yield point in pounds per square inch.
R = Absolute reduction, relative to the origin of the strain-hardening line (per cent reduction expressed as a decimal).
r = Test or working reduction, relative to the specific initial yield point (per cent reduction expressed as a decimal).

Written Discussion: By R. L. Templin, chief engineer of tests, research laboratories, Aluminum Co. of America, New Kensington, Pa.

In commenting on this timely paper, it may be pointed out first that the apparatus gives load-deformation or load-extension curves and not stress-strain curves. This distinction should be made in line with the definitions of stress and strain occurring in the Standards of the A.S.T.M.

The authors pointed out that one source of trouble with autographic apparatus of the type described, involving the use of a cord, is the elastic stretch which invariably occurs in such cords. In our own laboratories we have also found trouble from the inelastic stretch in such cords. Again, the errors resulting from the inertia of the weights usually attached to such cords are mentioned. These difficulties gave us so much trouble that we decided to abandon the use of cords in our more recent autographic apparatus, which has been described elsewhere.[4]

In view of the authors' statement concerning the errors resulting from the use of cords, it is somewhat difficult to understand their statement on page 580, second paragraph, wherein they speak of "two different instruments, which have proved to be capable of producing accurate stress-strain curves"—followed by the next sentence wherein the function of the cord is explained.

Contrary to the statement near the bottom of page 580, it has been found quite practical to design autographic extensometers that will give any mag-

[4]A.S.T.M. *Proceedings* for 1932.

nification desired from two to sixteen thousand, whose design involves the use of a screw micrometer.

For studying the deep-drawing characteristics of certain steels, the device described by the authors appears to be admirably suited and they are to be complimented on its efficiency and simplicity, both extremely desirable qualities in any such instrument. It must be pointed out, however, that there are other requirements for similar instruments in the testing of metals which in all probability cannot be adequately met by the apparatus described. Attention is particularly called to the determination of the elastic properties of metals, using the tensile test.

Numerous investigators have pointed out the effects of size and shape of specimen on the elongation values, using a constant gage length. I would like to ask the authors whether or not these effects are reflected in the shape of complete load extension diagrams, thus making interpretations difficult when different thicknesses of specimens are compared.

The troubles mentioned on page 594 in explaining Fig. 14, are largely occasioned by the fact that the apparatus described only registers deformation in a positive direction, that is, does not follow when contraction of the gage length occurs. This trouble has been overcome by the apparatus developed in the Aluminum Research Laboratories, previously referred to.

The use of the term "true" stress in the testing of metals sooner or later tends to get the investigator into trouble. By taking certain liberties with the size and shape of test specimen, the apparent stress required to break the specimen can be altered between very wide limits. For example, if we were to take a ½ inch diameter specimen and turn a sharp "V" groove around the center of the specimen, the load required to break the specimen, divided by the area of the specimen at the bottom of the groove, would give a stress value appreciably higher than could be obtained when using the normal testing procedure. Such a result would appear to raise the question as to just what is the actual strength of the material and at the same time cast considerable doubt on any statement as to the value of the "true" stress in the material. Would not the term "actual" be perhaps more definitive of the stress obtaining in the specimen, rather than the term "true"? The stress value for any given load, as ordinarily determined, might then be defined as "nominal".

From the data given in Fig. 15, page 594, it would appear that the tensile strength of the cold-rolled material might well be defined by the equation:

$$T = 37{,}500\ (1 + 1.64\ R)$$

wherein

T = the tensile strength for any given amount of cold rolling
R = the reduction in cross sectional area expressed as a decimal.

Values obtained from this equation not only check the ultimate strength values indicated in Fig. 15, but show a reasonably good agreement with the values indicated in Fig. 19, on page 595. In spite of this apparent check, however, the writer is inclined to agree with the authors, in that the plastic part of the

actual load deformation curve is not a satisfactory measure of the rate of strain hardening of the material.

Written Discussion: By Dr. Ing. W. Kuntze, Berlin-Dahlem, Germany.

The procedure described is valuable in making an accurate determination and valuation of the elongation curve in the tensile test. The writers are to be congratulated on not having taken the position that the uniform elongation is determined as accurately as possible by means of their equipment, but that the numerical values—which are not at all general—have a special significance.

The uniform elongation is more or less included in the per cent total elongation, depending on the definite gage length. High uniform elongation is not always an advantage to the material. Frequently, the plastic properties are better when the uniform elongation is small. Detailed physical tests, which because of lack of room unfortunately cannot be presented here, are to be found in my book "Kohäsionsfestigkeit" (Mitteilungen der deutschen Materialprüfungsanstalten, Reprint XX, Published by Julius Springer, Berlin Linkstrasse 23-24). In it a detailed analysis of the tensile test is carried through.

Authors' Closure

The authors appreciate the kind remarks of Joseph Winlock. The variables which he mentions are of importance and will, of course, be studied with the new extensometer.

Dr. Nadai suggests that the term "Lüder's lines" is to be preferred to "stretcher strains". While "Lüder's lines" is used frequently in foreign literature and to some extent in this country, the phenomenon is known to all sheet steel men as "stretcher strains" and the authors were attempting to speak the language of the deep-drawing sheet industry. Dr. Nadai has contributed a large amount of interesting and valuable work in the study of these "flow lines" and his recent book dealing with this subject is well known to the authors.

Dr. Kuntze has discussed the matter of uniform elongation. The authors agree with him that this quantity is more or less included in the per cent total elongation, but the latter is influenced by the gage length of the specimen. The separately determined uniform elongation is independent of this variable and therefore more characteristic of the material.

Mr. MacGregor referred to the difficulty in centering flat specimens in the testing machine and the effect of this on the upper yield point. The authors used special self-aligning grips which effectively overcame this difficulty. The curve presented by Mr. MacGregor shows very careful technique in obtaining the upper and lower yield point with a Martens extensometer, but has the limitation that the shape of the curve immediately after the upper yield point is not determined. The continuous autographic recorder overcomes this and gives a continuous record of the relationship between stress and strain.

We will discuss, in order, the various points raised by Mr. Crane. The first refers to the justification for a two to one relation between the true stress at A and at C in Figs. 17, 18, and 19.

The accompanying Fig. A is a schematic diagram of a true stress curve. Point A designates the beginning of local contraction and the line AC is drawn tangent to the curve at this point. The load P at any instant is dependent

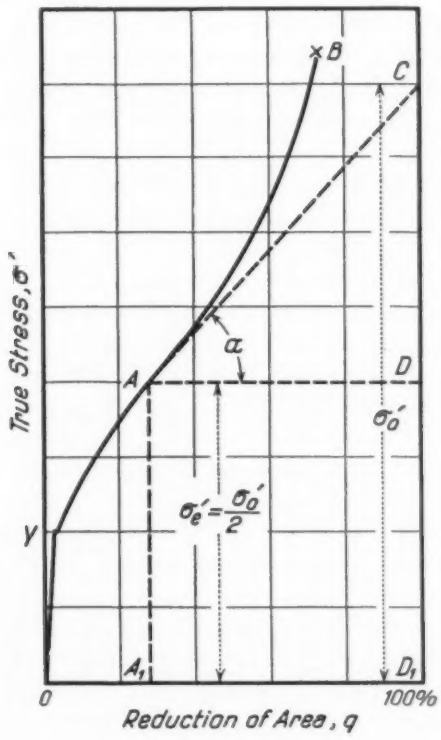


Fig. A

upon the instantaneous area of cross section F and the true unit stress σ' according to the equation:

$$P = F \cdot \sigma' \qquad (1)$$

Changes in the stress due to work-hardening and changes in cross section due to elongation of the specimen cause a change in load as follows:

$$dP = \sigma' \, dF + F \, d\sigma' \qquad (2)$$

The condition for the beginning of local contraction is:

$$dP = 0$$

If we use the subscript e to denote the particular values of the variables at Point A, we may write:

$$dP = \sigma'_e \, (dF)_e + F_e \, (d\sigma')_e = 0$$

or
$$\left(\frac{d\sigma'}{dF}\right)_e = -\frac{\sigma_e'}{F_e} \tag{5}$$

From the geometry of the figure:

$$\text{Tan } \alpha = \frac{d\sigma'}{dq} = \frac{\sigma_o' - \sigma'}{1 - q} \tag{6}$$

By definition:
$$q = \frac{F_o - F}{F_o} = 1 - \frac{F}{F_o} \tag{7}$$

and
$$dq = -\frac{dF}{F_o} \tag{8}$$

Substituting these values of q and dq in equation (6) we have:

$$-\frac{d\sigma'}{dF} F_o = \frac{\sigma_o' - \sigma'}{1 - 1 + F/F_o} = F_o \frac{\sigma_o' - \sigma'}{F} \tag{9}$$

and
$$-\frac{d\sigma'}{dF} = \frac{\sigma_o' - \sigma'}{F} \tag{10}$$

Substituting in equation (5): $\dfrac{\sigma_e'}{F_e} = \dfrac{\sigma_o' - \sigma_e'}{F_e}$ (11)

$$\sigma_e' = \sigma_o' - \sigma_e' \tag{12}$$

or
$$\sigma_e' = \frac{\sigma_o'}{2} \tag{13}$$

While the mathematical development of this relationship is perfectly straightforward, the authors wish to reiterate the statement made in the paper to the effect that point C has no practical significance because it seldom, if ever, lies on the actual work-hardening curve of the material.

Mr. Crane's method of plotting true stress curves as shown in his Figs. 2 and 3 seems to the authors to be quite arbitrary because he condenses his horizontal scale to make the straight portion of the work-hardening line coincide with the sloping line from the origin to S_x. Mr. Crane's deduction from his Figs. 2 and 3 to the effect that the "sheet sample, Fig. 18, was annealed to a softer and more plastic state than the bar sample, Fig. 17", is not borne out by the actual tensile data on these two specimens. As a matter of fact, the properties of these two materials are almost identical.

Property	Bar	Sheet
Lower Yield Point (Lbs./Sq.In.)	22,000	20,500
Upper Yield Point (Lbs./Sq.In.)	26,500	26,500
Tensile Strength (Lbs./Sq.In.)	42,000	39,500
Elongation (Per Cent in 2 Inches)	47.0	41.5
Reduction of Area (Per Cent)	75.0	63.1

We do not believe there is any justification for assuming that all material of a given analysis will show the same rate of work-hardening. Variation in structure, such as size and shape of grains and the nature of the constituents present due to variations in heat treatment certainly would have a profound influence.

In answering Mr. Templin's questions, the difficulties with cords mentioned in the paper refer to the older type extensometers in which the elongation was magnified by pulleys at the recording drum. In this case any stretch in the cord was also magnified. Both of the extensometers described in this paper magnify the elongation at the extensometer and the magnified motion is transmitted to the recording drum; hence the stretch of the cord is not magnified. The effect of size and shape of specimen on the characteristics of the autographic curve is a subject now under investigation. It is hoped that the results of this work may be published later.

The authors believe that the use of the term "true stress" is justifiable only as a matter of usage to denote instantaneous load divided by instantaneous cross sections. The term "actual stress" does not seem to offer material improvement, for as Mr. Templin has pointed out, it is difficult to determine the actual or true maximum stress which is effective during the tensile test.

The equation which Mr. Templin proposes for relating tensile strength to percentage cold rolling is open to the objection that it takes no account of variation in grain size, although it does represent quite accurately the behavior of the particular material upon which the tests recorded in Fig. 15 were made.

The authors appreciate the interest shown in this paper and wish to thank all those who have contributed to the discussion.

SOME OBSERVATIONS CONCERNING THE WIDMANSTATTEN STRUCTURE AND ITS FORMATION IN HYPOEUTECTOID STEELS

By A. P. Terrile

Abstract

This paper discusses experimental results obtained in a study of the formation of Widmanstatten structures in hypoeutectoid steels. The paper reviews briefly the theories advanced by several authorities on the subject.

Several experimental heat treatments on identical samples of steel are herewith reported and the results obtained are discussed and conclusions drawn in the light of the present investigation and the results obtained by other metallurgists.

ONE of the most interesting structures observed during the course of metallographic studies is that of the well known Widmanstatten formation. It was first discovered in 1808 by the French scientist Alois de Widmanstatten during an investigation of meteorites. This striking crystallographic arrangement of the constitutents has been encountered time and time again, being frequently associated with hypoeutectoid steels in the cast and forged condition. Colonel Belaiew[1], Dr. Krivobok[2] and Dr. Sauveur,[3] eminent metallographic authorities have been responsible for the principal theories concerning Widmanstatten formations in steel. However, it is an interesting fact that the theory held by Colonel Belaiew differs to a considerable degree with that of the other two scientists. Although all are in accord in the development of coarse austenite grains prior to cooling, Belaiew is of the opinion that the steel should be cooled slowly through the granulation zone and fairly rapidly (e.g., air cooling) through the zone of secondary crystallization. On the other hand, both Dr. Sauveur and Dr. Krivobok have succeeded in producing some excellent examples of Widmanstatten structures by

[1]"On the Genesis of Widmanstatten Structure in Meteorites and in Iron-Nickel and Iron-Carbon Alloys," by Colonel N. T. Belaiew.

[2]V. N. Krivobok, "Secondary Crystallization in Iron-Carbon Alloys," Transactions, American Society for Steel Treating, Vol. VII, April, 1925.

[3]"The Metallography and Heat Treatment of Iron and Steel," Second Edition, by Albert Sauveur.

The author A. P. Terrile is a member of the society and is associated with the metallurgical department of the Pittsburgh Crucible Steel Co., Midland, Pa.
Manuscript received January 31, 1933.

cooling slowly through the granulation zone and the secondary zone.

Colonel Belaiew's method of cooling was based upon his belief that during critical transformation a migration of ferrite took place from the interior of the grains toward the boundaries. A relatively fast cooling would entrap the ferrite along the cleavage planes, the resulting structure being of Widmanstatten type. A slow cooling would promote the cellular network structure, time being afforded for the proeutectoid ferrite to reach the boundaries. Dr. Krivobok has offered considerable evidence in his paper[2] to substantiate his theory of Widmanstatten formation by slow cooling. The theory summarized states that during cooling upon critical transformation, the ferrite is rejected from solid solution, first along the boundaries of the austenite grains. As cooling proceeds, the transformation continues with more alpha iron crystallizing from the boundaries into the interior of the grains along the cleavage planes. Hence, in direct opposition to Colonel Belaiew, the consequence would be the development of Widmanstatten structures upon slow cooling, and structures of the network type by relatively fast cooling. Dr. Sauveur[4] is in accord with the theory of Dr. Krivobok.

A salient point is, that regardless of the quite opposite views held, the methods of Colonel Belaiew and Dr. Krivobok have both succeeded in producing Widmanstatten structures. In this connection, it must be considered that the steels experimented with were plain carbon analyses, with carbon contents on the higher side of the hypoeutectoid range.

The hypoeutectoid range of annealed plain carbon steels may conveniently be divided into two structural classifications, selecting 0.35 per cent carbon arbitrarily as the line of demarcation. Above this carbon content the amount of free ferrite considerably diminishes, the structures becoming of eutectoid character. Below this point the structures are characterized by the predominance of the ferrite constituent.

Studying the methods of treatment followed by Colonel Belaiew and Dr. Krivobok, it is found that the main difference was in the rate of cooling the steels through the secondary zone, both having conducted the cooling slowly through the granulation zone. This part of the cooling is believed to have been of marked influence in their formation of Widmanstatten structure.

A consideration of several of the established principles of metal-

[4]Dr. Albert Sauveur, "Austenite and Its Decomposition," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1929, p. 199.

lography will serve to clarify the explanation for this premise. With increasing carbon content, the temperature of the Ar_3 point becomes progressively lower and lessens in intensity. This condition is further affected to a marked degree by the rate of cooling. Accelerating the cooling depresses the Ar_3 temperature. Retarding the rate of cooling through the granulation zone would allow the Ar_3 point to occur at a higher temperature. However, the maximum temperature of transformation attainable, even by infinitely slow cooling, theoretically would not be higher than the equilibrium transformation temperature as established by the chemical composition of the steel.

In the case of Colonel Belaiew's method, the slow cooling through the granulation zone induced the occurrence of the Ar_3 point at a temperature sufficiently high to materially intensify and accelerate the transformation reaction. The austenite grains had transformed in all likelihood almost simultaneously at the boundaries and along the cleavage planes. The air cooling through the secondary zone permitted no time for appreciable coalescence of the ferrite constituent, the Widmanstatten structure thus being sharply defined. Dr. Krivobok's samples, although exhibiting excellent examples of Widmanstatten formations, showed more ferrite coalescence due to their slower cooling through the secondary zone. It should be recalled that Dr. Krivobok's coolings were conducted from the melt. The intimate contact of the steels and molds insured a uniform cooling rate throughout. Slow cooling rates under these conditions introduced no appreciable thermal gradient between the steel and the cooling medium.

Considerable difference is known to exist between the cooling rates of charges and furnaces. This is particularly apparent during the early cooling stages. The relation between the size of the charge and furnace employed is obviously important. As the charge weight increases per given furnace size, the thermal gradient between them decreases, both tending toward cooling uniformly. In most commercial instances of undisturbed furnace cooling from high temperatures, during the first part of the cooling the charge loses heat more rapidly than the furnace. As cooling continues, a temperature is reached at which both are in equilibrium. From this point the charge and furnace cool uniformly. The factors described are believed to have had great influence in promoting the network type of structure often observed in the higher carbon hypoeutectoid steels when furnace-cooled from high temperatures.

Hypoeutectoid Steels of Eutectoid Character

In order to demonstrate these views, several experimental heat treatments were conducted on identical samples of S.A.E. 1040 and 1050 steel. The analysis of the steels, size samples employed, and the treatments are given in detail in Table I.

Table I

Steel	Sample Size	Analyses: Carbon	Manganese	Phosphorus	Sulphur	Silicon	Treatment	Heated Degrees Fahr.	Time at Temp.	Rate of Cooling: Granulation Zone	Rate of Cooling: Secondary Zone
S.A.E. 1040	2" Sect. of 4x4" billet	0.41	0.56	0.018	0.026	0.14	A	2200	2 hours	Air	Air
S.A.E. 1040	2" Sect. of 4x4" billet	0.41	0.56	0.018	0.026	0.14	B	2200	2 hours	Unretarded Fce.	Unretarded Fce.
S.A.E. 1040	2" Sect. of 4x4" billet	0.41	0.56	0.018	0.026	0.14	C	2200	2 hours	100° F. per hr. to 1500° F.	Air
S.A.E. 1040	2" Sect. of 4x4" billet	0.41	0.56	0.018	0.026	0.14	D	1800	2 hours	100° F. per hr. to 1500° F.	Air
S.A.E. 1050	2" Sect. of 4x4" billet	0.54	0.63	0.015	0.022	0.17	E	1800	2 hours	100° F. per hr. to 1500° F.	Air
S.A.E. 1050	2" Sect. of 4x4" billet	0.54	0.63	0.015	0.022	0.17	F	1800	2 hours	100° F. per hr. to 1500° F.	Unretarded Fce.

Note—All steels were coarse-grained normal.

The object of treatment A was to produce considerable lowering of the Ar_3 temperature by a comparatively rapid cooling. The structure obtained, as shown in Fig. 1, consisted of a fine network of free ferrite around coarse sorbite grains. The experiment also corroborated Dr. Krivobok's theory of ferrite formation occurring first at the grain boundaries, rather than in the interior of the grains as proposed by Colonel Belaiew.

Treatment B was performed to show the persistence of the network type of structure under conditions of ordinary furnace cooling. The furnace was of the gas-fired type employed for hardening of high speed steel. The cooling from 2100 degrees Fahr. to the discharge temperature of 800 degrees Fahr. took 8½ hours. The structure, as illustrated by Fig. 2, was of pronounced network character, with considerable free ferrite in a matrix of lamellar pearlite.

The purpose of treatment C was to overcome the thermal gradient present under undisturbed furnace cooling. To accomplish this, the cooling through the granulation zone was considerably re-

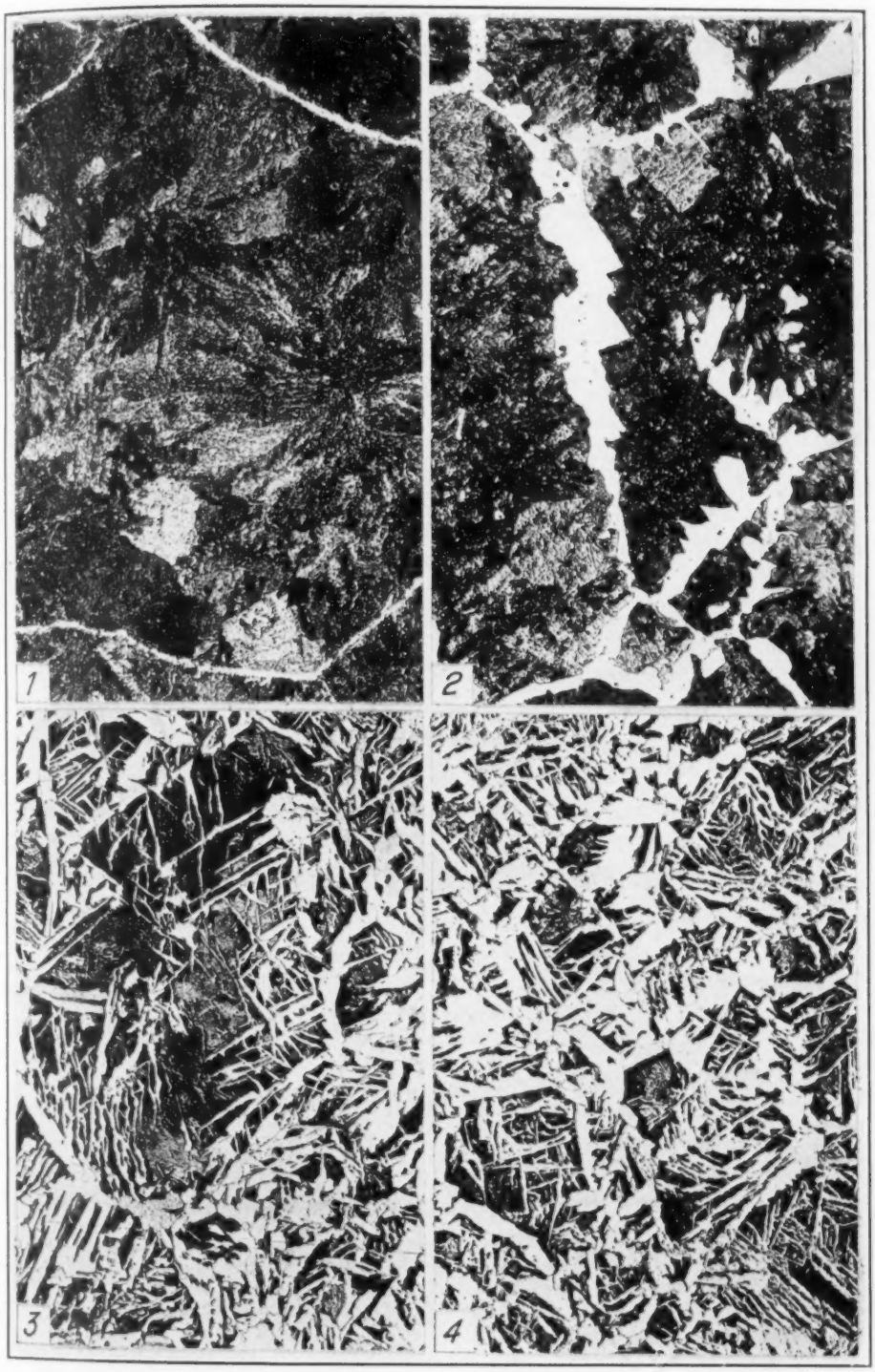


Fig. 1—Microstructure After Treatment A on S.A.E. 1040 Steel. Nital. × 100.
Fig. 2—Microstructure After Treatment B on S.A.E. 1040 Steel. Nital. × 100.
Fig. 3—Microstructure After Treatment C on S.A.E. 1040 Steel. Nital. × 100.
Fig. 4—Microstructure After Treatment D on S.A.E. 1040 Steel. Nital. × 100.

tarded, being conducted at a rate of 100 degrees Fahr. per hour. The steel was air-cooled through the secondary zone to avoid the possibility of excessive ferrite coalescence. The steel contained a sharply defined Widmanstatten structure as shown by Fig. 3.

In re-heated steels, the maximum heating temperature has such a marked influence upon the temperatures of occurrence of the Ar points that this factor with relation to Widmanstatten formation could not be disregarded. It has been established that with higher heating temperatures the suppression of the critical range is greater per given cooling speed. Lower heating temperatures, therefore, would be expected to result in higher transformation temperatures upon cooling. The consequence should be acceleration of the transformation reaction at Ar_3 with more rapid ferrite formation. In order to show the influence of a lower heating temperature upon the development of Widmanstatten structure, treatment D was conducted. The structure developed was of pronounced Widmanstatten type as illustrated in Fig. 4. Evidence of a higher Ar_3 temperature is shown by the abundance of free ferrite and marked coalescence of this constituent which had occurred, particularly at the grain boundaries. The air cooling through the critical range apparently prevented appreciable agglomeration of the ferrite formed along the cleavage planes.

Repeating this experiment (Treatment E) on a sample of S.A.E. 1050 steel produced the structure in Fig. 5. The free ferrite was in Widmanstatten arrangement, but considerably less of this constituent was present due to the higher carbon content. An additional sample of this steel treated similarly, with the exception of furnace cooling through the critical range (Treatment F) showed the Widmanstatten structure completely masked by ferrite coalescence as illustrated by Fig. 6.

Hypoeutectoid Steels of Ferrite Character

With the plain carbon hypoeutectoid steels of ferritic character, as carbon diminishes with correspondingly higher Ar_3 temperatures, the tendency toward ferrite coalescence becomes more pronounced. This may be strikingly illustrated by a study of the decarburized surface of a medium high carbon steel after undisturbed furnace cooling from a high temperature. In Fig. 7 is shown the gradation of coalesced rounded ferrite grains in the decarburized zone to network

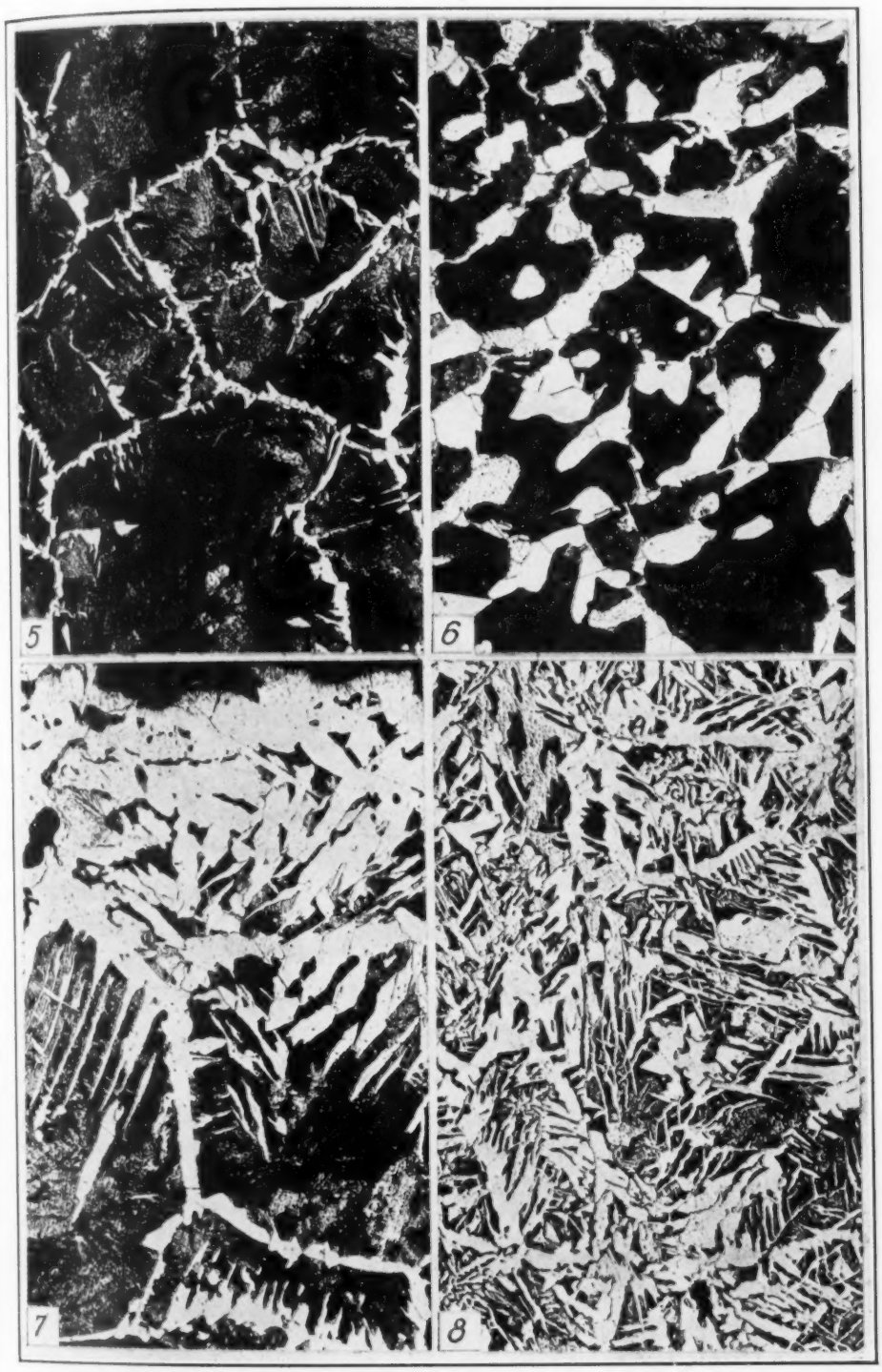


Fig. 5—Microstructure After Treatment E on S.A.E. 1050 Steel. Nital. × 100.
Fig. 6—Microstructure After Treatment F on S.A.E. 1050 Steel. Nital. × 100.
Fig. 7—Microstructure Showing Edge of Specimen Used for Treatment B. × 100.
Fig. 8—Microstructure of S.A.E. 1025 Steel Treated as Shown in Table II. × 100.

formation in the interior. The intermediate area was of Widmanstatten structure. This particular example was from the edge of the specimen used in treatment B.

The development of Widmanstatten structure in these steels depends mainly on directing the treatment to avoid excessive ferrite crystallization and agglomeration. For example, as the carbon content diminishes to zero from any given heating temperature well over

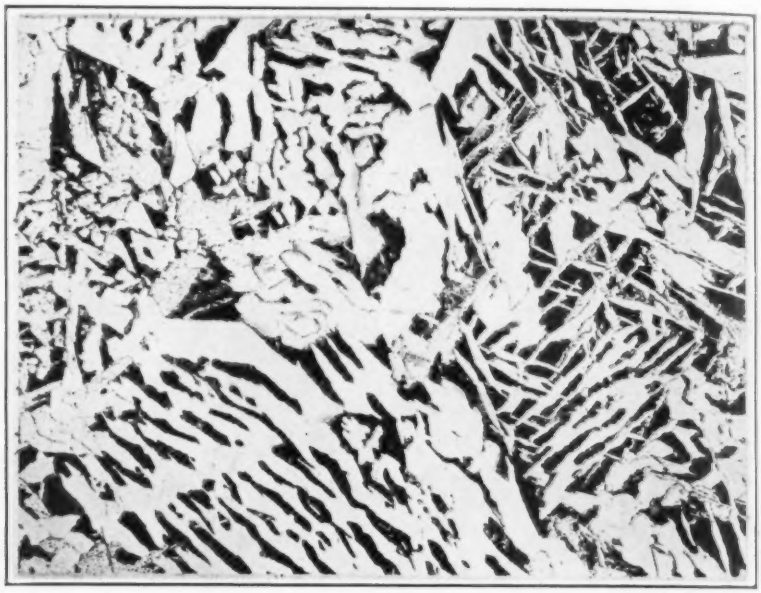


Fig. 9—Microstructure of S.A.E. 1025 Steel Treated as Shown in Table II. Nital. × 100.

the critical range, the rate of cooling theoretically should be proportionately accelerated. An instance of this was the development by Dr. Sauveur and Dr. Chou[4] of Widmanstatten structure in carbonless iron by drastic quenching from a high temperature.

The carbon range between 0.20 to 0.30 per cent in plain carbon steels is quite adaptable to the formation of Widmanstatten structures. Some latitude may be allowed in the cooling rates from high temperatures. Practically any heating temperature over 1800 degrees Fahr. followed by air cooling will produce sharply defined Widmanstatten structures. In fact, with temperatures over 1900 degrees Fahr. the formation has been observed after either air or furnace cooling. Figs. 8 and 9 illustrate these conditions in samples of S.A.E. 1025 steel. The greater coalescence of the free ferrite in the furnace-cooled steel should be noted. The detailed information concerning these treatments is given in Table II.

Table II

Steel	Sample Size	Analysis: Carbon	Manganese	Phosphorus	Sulphur	Silicon	Photomicrograph	Heat Treatment: Heated °F.	Time at Temp.	Cooled
1025	1⅜" Rd.	0.24	0.57	0.025	0.021	0.18	Fig. 8	2000	1½ hours	Air
1025	1⅜" Rd.	0.24	0.57	0.025	0.021	0.18	Fig. 9	2000	1½ hours	Furnace

Note—The steel was coarse-grained normal.

Summary

A study of Dr. Krivobok's and Colonel Belaiew's methods of formation of Widmanstatten structure showed the main difference between them to have been the cooling of the steels through the secondary zone, both having conducted the cooling very slowly through the granulation zone.

In the hypoeutectoid steels of eutectoid character the rate of cooling through the granulation zone was shown to be a factor of marked influence toward the development of Widmanstatten structure. In this connection, there was discussed the cooling of Dr. Krivobok's steels from the melt with consequent minimized suppression of the Ar_3 point, due to uniform cooling resulting from the contact of the steels and molds.

The persistence of network type structures in re-heated steels furnace-cooled was shown to be in a large part due to the differential cooling of the charge and furnace. The more rapid cooling of the charge during the early cooling stages induced a suppression of Ar_3.

A controlled rate of cooling through the granulation zone was demonstrated to overcome the suppression of the Ar_3 point usually encountered under conditions of undisturbed furnace cooling. Widmanstatten structure in S.A.E. 1040 steel was developed from a comparatively low heating temperature of 1800 degrees Fahr. by a close control of the cooling rate through the granulation zone.

The cooling rate through the secondary zone in relation to Widmanstatten structure was demonstrated to be a factor of importance in determining the extent of ferrite crystallization and coalescence.

The development of Widmanstatten structure in hypoeutectoid steels of ferritic character was shown to depend mainly on directing the treatment in such manner as to avoid excessive ferrite crystallization and agglomeration.

In the range of 0.20 to 0.30 per cent carbon, Widmanstatten structure was produced by air or furnace cooling from a high heat.

Discussion

It was interesting to note that with the experimental examples of higher carbon hypoeutectoid steels, the treatments which had produced the most pronounced Widmanstatten structures followed somewhat the method proposed by Colonel Belaiew, yet the evidence was overwhelmingly in favor of Dr. Krivobok's fundamental hypothesis of ferrite formation from austenite.

In this respect, the fact that these steels had been re-heated and not cooled directly from the melt introduced such additional factors as the maximum heating temperature, time held at temperature, and rate of cooling, all of which had material effect upon the Ar_3 point.

The development of Widmanstatten structure as carbon increased with diminishing ferrite content had apparently depended upon the temperature of the Ar_3 point as well as the rate of cooling through the transformation range. It is believed that the transformation reaction was accelerated by the occurrence of austenite decomposition at a higher temperature. This was the main purpose of retarding the cooling rate through the granulation zone. The importance, in many cases, of a closely controlled cooling and definite knowledge of the rate of cooling toward the attainment of a specific structure cannot be over-emphasized. After all, the term "slowly cooled" is vague and purely relative. To simply state that a steel had been furnace-cooled conveys but little knowledge concerning the actual cooling rate that had occurred.

For example, in the automotive field the factor of machinability alone requires a knowledge of every detail of temperature, time and cooling rates involved in the actual annealing process. The development of annealing cycles has opened a fertile field for the development of specific structures.

Undoubtedly, many other factors bear an important part in the attainment of a definite structure. With chemical composition as the fundamental background, uniformity, as evidenced by the extent of dendritic segregation, the degree of normality, grain size, all bear an important relation to transformation temperatures and transformation reactions.

The Widmanstatten structure, although of no considerable commercial value, was chosen in the higher carbon range of hypoeutectoid steels as a structure of specific type attainable only by careful and closely controlled treatment.

A SIMPLE CUTTING TOOL FOR MEASURING PRESSURES IN THE DIRECTION OF CUT

By O. W. Boston and C. E. Kraus

Abstract

This paper describes a special tool holder by which the cutting resistance or tool pressure is determined from the tool point deflection as read on an indicating gage. The tool permits easy and rapid determination of that component of tool pressure which is in the direction of cut. The tool is simple and rugged in construction, installed as readily as any tool in a lathe, planer, and shaper, and is useful in comparing the machining properties of various metals or the same metal under different conditions, in determining the relative effect of cutting fluids or tool angles on power required, and in determining force or power equations in terms of depth of cut and feed for specific metals and cutting conditions. Results of a variety of types of tests demonstrate the use of the device for rapid comparative studies.

BECAUSE of the increasing demand for results of a comparative nature to indicate the relative machining properties of different metals or a given metal under different conditions, a small tool has been developed which may be used as an ordinary cutting tool in the standard tool posts of lathes, planers, and shapers.

It is recognized that, of the many methods of measuring machinability, one giving tool life is of the most practical value and the type of information most commonly required. Tool-life tests are, however, often not only difficult but expensive to obtain. Other types of tests used in determining the relative machinability of materials have been used, such as the torque, thrust, and power developed in drilling, the force on a planer or lathe tool as measured by a large expensive dynamometer, the time for a given drill under a constant feeding load to penetrate a given distance, etc. These methods all

A paper presented at the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, who are members of the society, O. W. Boston is director, Department of Engineering Shops at the University of Michigan, Ann Arbor, Mich., and C. E. Kraus holds the appointment of student assistant to him. Manuscript received April 9, 1932.

have certain objections in that the results, as in the case of drill penetration, do not always indicate the most favorable machining conditions, or that the devices are expensive, difficult to operate except by trained personnel, and require considerable time.

The device described in this paper is intended primarily for comparative tests of a routine nature, such as the testing of various specimens of steel screw stock for uniformity and ease of cutting. It is not intended for use as a piece of laboratory test equipment,

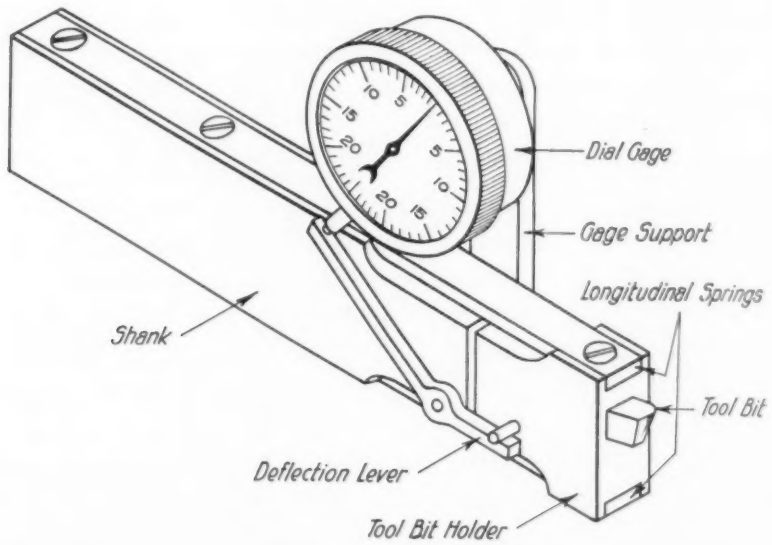


Fig. 1—Tool Dynanometer Used to Measure the Cutting Force in the Direction of Cut.

although, if intelligently handled, it will give favorable comparative or absolute results when used under carefully standardized operating conditions.

The tool as illustrated by the line diagram in Fig. 1 is designed to fit into an ordinary tool post of a lathe, planer, or shaper. The tool consists principally of a shank, a bit holder, and a deflection indicating mechanism. The shank and bit holder were machined as a single piece and then cut in two. Set into a longitudinal groove in the top and bottom of the shank and holder so as to be flush with the surface and to separate, at a short distance, the tool holder from the shank, are two high carbon steel springs which permit a vertical motion of the bit holder perpendicular to the longitudinal axis of the shank. By means of a lever shown in Fig. 1, any vertical movement of the tool bit holder relative to the shank, which is clamped rigidly

in the tool post, is transmitted to the dial indicator fastened to the shank.

In order to make the device as rugged as possible, the springs were made quite heavy and the lever was designed to amplify the deflections of the tool point. The holder takes a ¼-inch square tool

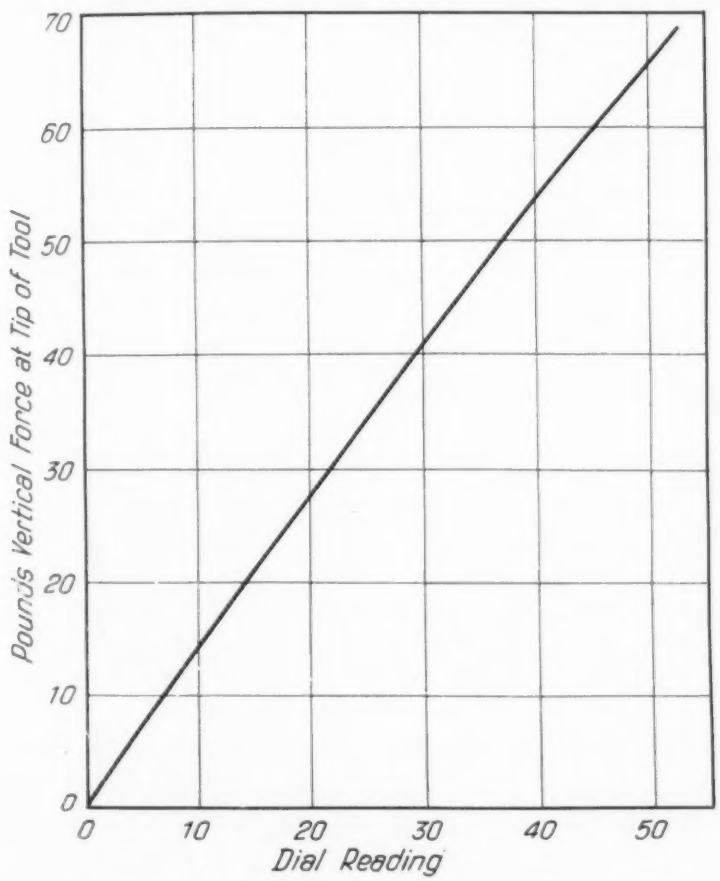


Fig. 2—Calibration Curve for Tool Dynamometer—Tool Tip Projecting Forward $\frac{9}{32}$ Inch.

bit which, as in ordinary tool holders, is held at a 15-degree back-rake angle.

The calibration curve of the holder showing the relation of the dial gage reading as a function of the tool load is shown in Fig. 2. This curve is approximately a straight line. The calibration was carried out with the tool point projecting 9/32-inch beyond the end of the holder, but since the device is essentially a parallel linkage, the projection of the tool bit has practically no effect on the calibration curve. The curve could be determined for several times the maxi-

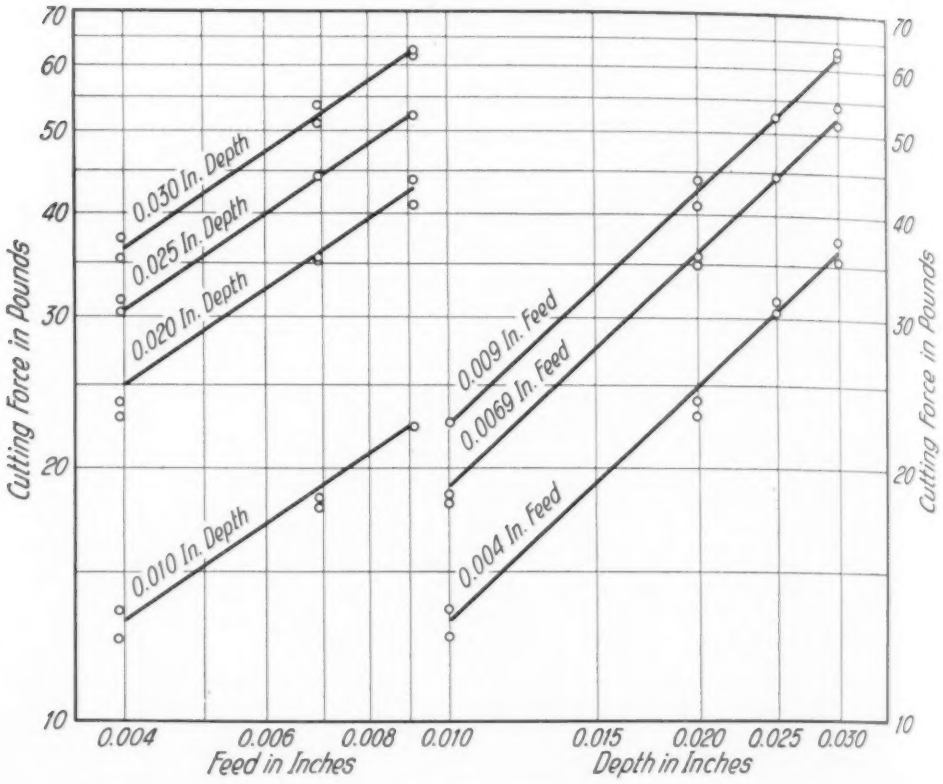


Fig. 3—Tangential Cutting Force for Light Turning Cuts on Cold-Rolled Low Carbon Steel. Dynamometer Tool Cutting Dry. Bar 2.938 Inches Turned to 2.5 Inches in Diameter. Initial Cutting Speed 64 Feet per Minute. High Speed Steel Tool Bit "A" Used. Side Rake 0 Degrees. Back Rake 15 Degrees. End-Cutting Angle 6 Degrees. Front and Side Clearance 6 Degrees. Nose Radius 0.010 Inch. Setting Angle 90 Degrees.

mum deflection shown, as the lever ratio amplified the deflection about three to one on this model. Also, by modifying the tool springs, practically any moderate range of tool pressures could be measured.

In order to demonstrate the usefulness and adaptability, as well as the limitations of this conveniently applied tool, the results of a number of different types of tests are presented.

Effect of Various Combinatons of Feed and Depth of Cut on The Tangential Cutting Force

Turning low carbon steel—After making the tool dynamometer, tests were first run designed primarily to ascertain the best range of feeds and depths of cut for subsequent standardized tests. A bar of low carbon cold-rolled steel taken from stock was centered and trued up, after which it measured 2.5 inches in diameter. It was run at 98 revolutions per minute, which gave an initial surface cutting speed

of 64 feet per minute. The tool bit used was ¼ inch square in section and was of high speed steel. It was ground so as to have no side-rake angle, a 15-degree back-rake angle, a 6-degree end cutting angle, a 6-degree front and side-clearance angle, a setting angle of 90 degrees, (that is, the axis of the tool and the cutting edge were at right angles to the axis of the work), and an 0.010 inch nose radius. Bits of this particular size and shape are designated as A.

For each depth of cut of 0.010, 0.020, 0.025, and 0.030 inch, feeds of 0.004, 0.0069, and 0.0091 inch were used. Two identical series of tests were run, the results of which are shown plotted as tangential cutting force in pounds over the variable on log-log paper in Fig. 3. The two series of tests appear to compare favorably with one another. It is apparent from the calibration curve, Fig. 2, that even greater depths of cut and feeds might have been taken.

The surface of the metal cut was very smooth and showed sharply defined and unbroken feed helix lines. The vibration of the dial indicator needle was not found to be objectionable. Later tests on a cast semi-steel bar gave considerable vibration of the gage needle and made accurate readings difficult to obtain.

The results of the above preliminary tests as shown in Fig. 3 indicate that the tool pressure is a function of some power of the feed and depth. The slopes of the lines have been measured and indicate the following equation:

$$P = 38{,}700\ F^{0.67}\ D^{0.94}$$

in which P is the tangential cutting force, C is a constant for the material cut and the tool when cutting dry, F is the feed, and D is the depth of cut in inches. It is apparent that, for the range of feed and depths of cut covered by this equation, metal can be removed much more efficiently with coarse feeds than with fine feeds and that the depth of cut has very little effect on the efficiency. P in pounds was 44.5 for a feed of 0.007 inch and a depth of 0.025 inch.

Turning an annealed S. A. E. 3150 steel—Tests similar to those described above were repeated on an annealed S.A.E. 3150 steel which had been used in a number of other machinability tests.[1] Three series of tests were run in accordance with the information given in Fig. 4 where the data are shown plotted on log-log paper. The elongated points indicate the range covered by the vibrating dial of

[1] O. W. Boston and C. J. Oxford. "Performance of Cutting Fluids," *Transactions*, American Society of Mechanical Engineers, Vol. 54, No. 3, Feb. 15, 1932.

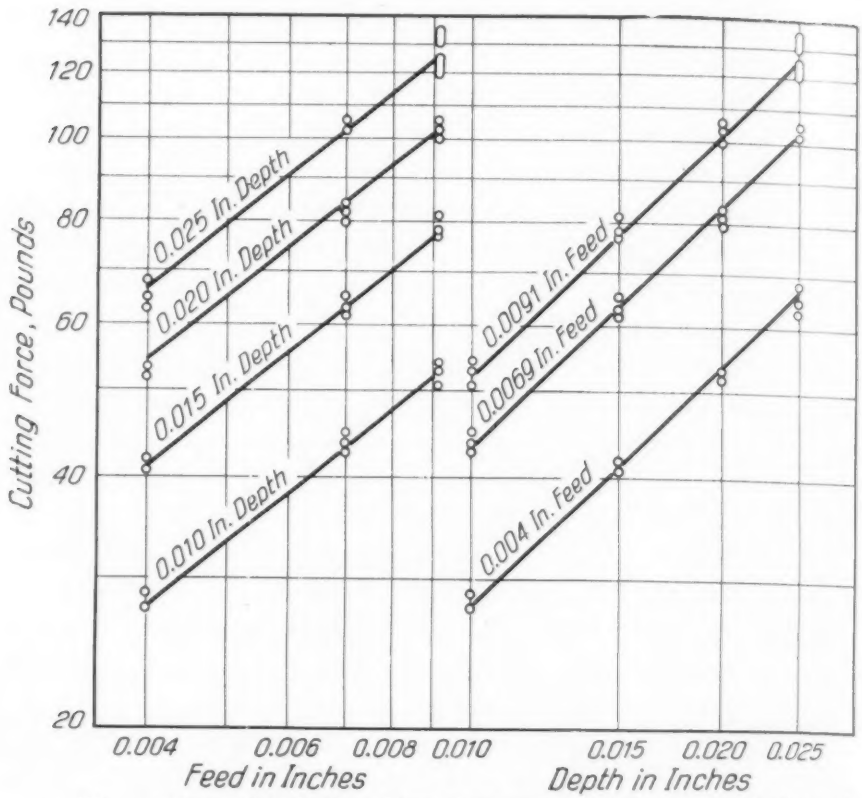


Fig. 4—Tangential Cutting Force Produced by Various Combinations of Feed and Depth of Cut on Turning an Annealed S.A.E. 3150 Steel. Dynamometer Tool Cutting Dry. Bar Turned to 1.733 Inches in Diameter. Speed of Cut 51 Revolutions Per Minute. High Speed Tool Bit "B" Used. Side Rake 14 Degrees. Back Rake 8 Degrees. Front and Side Clearance 6 Degrees. Nose Radius 0.010 Inch. Setting Angle 90 Degrees.

the tool. The "B" tool was used in these tests in which the back and side rake of tool "A" were changed to 8 and 14 degrees, respectively, as these angles had been used more often in other tests. Again, a close agreement in corresponding values is noted, and from the constant depth and constant feed lines the formula representing the cutting force as a function of the feed and depth of cut is found to be

$$P = 155{,}000\ F^{0.78}\ D^{0.94}$$

P in pounds was 102 for a feed of 0.007 inch and a depth of 0.025 inch. This equation is shown to agree very well with that obtained in planer tests on the same steel when cutting dry, as follows:

Turning tool dynamometer,
$P = 155{,}000\ F^{0.78}\ D^{0.94}$
Planer dynamometer,
$P = 128{,}200\ F^{0.78}\ D^{0.93}$

The constant of the turning tool dynamometer is 21 per cent higher than that of the planer dynamometer. The reason for this cannot be explained. It may be due to the fact that a slightly higher cutting speed was used in turning than in planing. Also, that there is a difference in the constant due to straight line cutting over turning. Check tests were run with a feed of 0.007 inch and a depth of cut of 0.025 inch with the tool used in the turning tests and with a tool ground and honed to the exact shape and condition of that used in the planer tests, and only a 3 per cent greater force in turning was found. The tool used in the planer tests was honed all over and had a 1/32 inch radius as compared to the unhoned tool used in turning with a 0.010 inch nose radius.

Taylor's formula when cutting steel was

$$P = C\,D\,F^{0.935}, \text{ in which } C = 230{,}000$$

but when cutting soft and hard cast iron was

$$P = CF^{0.75}\,D^{0.935}$$

for his ½, ¾, and 1¼ inch wide shank high speed steel round-nose tool, which agrees almost exactly with the authors' equation. Taylor's constants C were 45,000 for soft cast iron and 69,000 for hard cast iron.

An average for the planer-force equation above for all cutting fluids is

$$P = C\,F^{0.79}\,D^{0.95}$$

in which, for dry cutting, C = 128,200, and for the sulphurized mineral oil No. 10, C = 108,200. (See Table II).

The formulas for cutting force P, when turning the low carbon cold-finished steel and the annealed S.A.E. 3150 steel, are not in agreement regarding the exponent of the feed F, as 0.67 was obtained in the first case and 0.78 in the latter. This is due probably to the fact that tool A was used in the first case and tool B in the latter. These tools are described in the caption of Figs. 3 and 4.

Results From Tool Dynamometer Tests Compared With Those From Other Methods of Tests

In order to compare data taken with the tool dynamometer with machinability data obtained by other methods of tests and to show

Table I

Comparing Machinability Data of Four Methods of Tests
(For description of tests, See Fig. 5.)

Bar No.	Material	Planer Force in Pounds	Drill Torque in Ft. Lbs.	Milling Energy in Ft. Lb./Chip	Tool Dynamometer Force for Shaper
187A	Brass Screw Stock (Annealed)....	581	9	11.93	20.5
BB	Bearing Bronze	503	8	13.38	23.0
Al-31	Aluminum Alloy	648	11	9.34	23.0
11-1	Cast Iron	1022	17	18.23	33.0
MB	Manganese Bronze	750	23	16.3	37.5
414	Super-Free-Cutting Screw-Stock Steel		23.4	26.63	39.5
416	S.A.E. 1112 Cold-Drawn Steel ..	1475	24.5	28.53	43.5
Al	Axle Steel	1745	29.5	36.44	56.5
Tl	Tool Steel	2244	37	46.05	65.5

the adaptability of the new tool for use in a shaper, the following tests were run.

Nine test bars 12 inches long were selected covering a variety of metals, for each of which results of various other machinability tests were available.[2] Each bar in turn was clamped in a shaper vise and the surface smoothed with another tool.

The tool dynamometer was inserted and the shaper set at 10½, the lowest number of strokes per minute, and a length of stroke of 16 inches. This corresponded to a cutting speed of approximately 20 feet per minute. The feed ratchet was set at one notch, which was equivalent to approximately 0.006 inches per cut. A very light surfacing cut was taken with the dynamometer tool in order to get a good zero reading for depth, after which the tool was fed to a depth of 0.010 inch as indicated on a dial gage. Readings on all metals were obtained under this condition with tool A. The tool left a very good surface on all metals and, except when cutting cast iron, no objectionable vibration was noted. The nine metals tested are listed in Table I, together with the force on a standardized planer tool, the torque on a ¾-inch diameter drill, the milling energy per chip of a standardized milling cutter, and the dial readings on the new tool.

A description of the materials and other methods of tests is given in detail in a previous paper.[3] These data are shown plotted over the

[2]O. W. Boston and C. J. Oxford, "Performance of Cutting Fluids in Drilling Various Metals," *Transactions*, American Society of Mechanical Engineers, Vol. 53, 1931.

[3]O. W. Boston, "Methods of Tests for Determining the Machinability of Metals in General, With Results", TRANSACTIONS, American Society for Steel Treating, Vol. 16, November, 1929, p. 659-710.
O. W. Boston, "Machining Properties of Some Cold Drawn Steels", *Transactions*, American Society of Mechanical Engineers, Vol. 53, MSP-52-6, 1930.

materials arranged as abscissa from left to right in order of decreasing values of force on the tool dynamometer in Fig. 5. The comparative accuracy of the device is immediately apparent, and it is

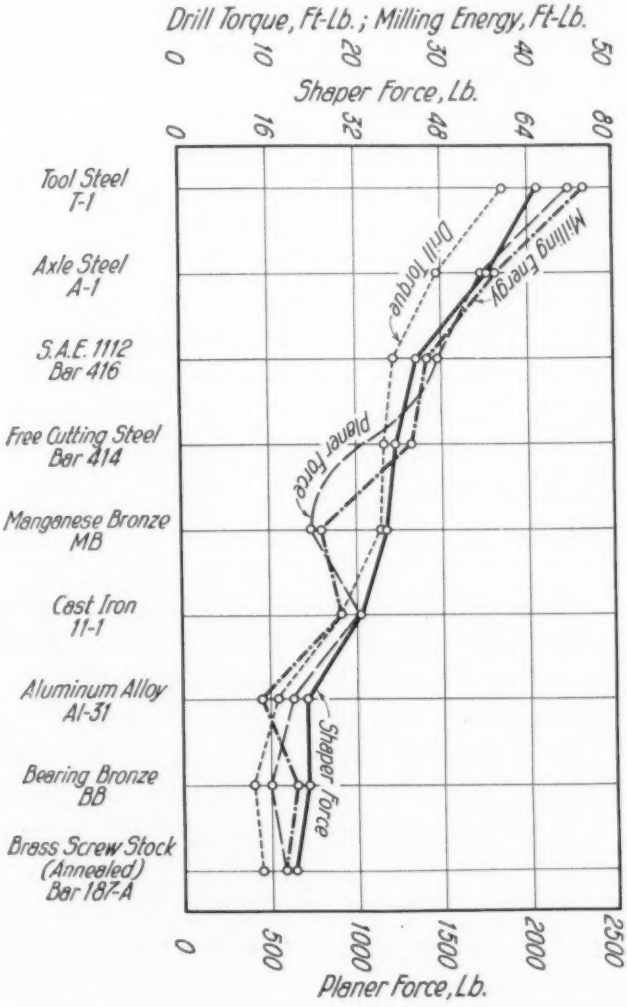


Fig. 5—Comparing Machinability Data of Four Methods of Tests on Nine Different Metals. All Tests Run Dry.

significant that the total time required to prepare the specimens and make these tests was only about five hours. With but one or two exceptions, the four curves shown in Fig. 5 agree very well. The first four metals from the left, consisting of tool steel T1, axle or medium carbon steel A1, free-cutting S.A.E. 1112 steel 416, and a free-cutting steel 414, respond practically alike to all four methods of tests. The planer-force curve for bar 416 appears to be slightly high. The manganese bronze MB seems to show low values for the

planer-force and milling-energy curves and rather high values for drill-torque and shaper tool dynamometer. The milling-energy curve for the aluminum alloy Al-31 seems to be low. In general, however, these various ratings compare favorably. From this it seems possible that machinability ratings of the tool load type may be obtained quickly and with little expense by the tool dynamometer.

The Influence of a Cutting Fluid

The adaptability of the tool dynamometer to compare the influence of various cutting fluids from a power standpoint for a given material is shown by the following tests.

Cutting low carbon steel—A low carbon cold-rolled steel was cut with eleven different cutting fluids. These eleven cutting fluids were selected as representing various types commonly used. They have been reported previously in connection with planing and drilling,[1] and milling[4] various metals. They are listed with their various properties in Table II.

The bar of low carbon steel was first centered and a light cut taken to remove the irregular surface. Tool type A was used in the tool dynamometer. The tool operated at a set depth of cut of 0.010 inch and a feed of 0.0091 inch. Each cutting fluid in turn was applied by hand from a large oil can in a steady stream at the point of cutting. The dial indicator was read during the cut. When changing from one cutting fluid to another, the tool was not withdrawn from the work, although the work was cleaned thoroughly, after which the cut was allowed to continue long enough with the new oil to eliminate the possibility of any influence of the cutting fluid previously used. About one inch of length of bar was found to be ample for a single test.

Three series of tests were made, each time changing the order of application of the cutting fluids, and after each test the bar was measured with a micrometer to determine the actual depth of cut. Cuts 1 and 3 were made with a depth of cut of 0.010 inch, but test 2 was run with an actual depth of cut of 0.0115 inch, so that the indicator readings are proportionately high.

The results of these tests are shown graphically in Fig. 6. The lines representing the results of each test show rather consistent re-

[4]O. W. Boston and C. E. Kraus. "Elements of Milling," presented at the annual meeting of the American Society of Mechanical Engineers, in New York City, November 30, 1931.

Table II Properties of Cutting Fluids Used

Table II

Properties of Cutting Fluids Used

[From "Performance of Cutting Fluids," by O. W. Boston and C. J. Oxford, Trans. A.S.M.E., vol. 53 (1931)]

No.	Composition	Base of Mineral Oil	Per Cent Compounding by Analysis	Viscosity at Deg. Fahr. 100	Viscosity at Deg. Fahr. 130	Viscosity at Deg. Fahr. 210	A.P.I. Gravity at 60 Deg. Fahr.	d Specific Gravity
1	Dry cutting	.....	.....	...	...	....	....	.....
2	1½ per cent by weight of borax in water ..	.....	1.19 borax	...	...	....	....	.....
3	1 part soluble oil in 50 parts water	.....	2.3 soluble oil	31	...	....	....	.....
4	1 part soluble oil in 10 parts water	.....	8.37 soluble oil	32	...	....	....	.....
5	No. 1 lard oil	.....	12.23-13.6 F.F.A.[1] 86.4 fat	200	110	....	23.7	0.9117
6	Light mineral oil	Mixed	.....	111	69	40.5	23.5	0.9129
7	Heavy mineral oil	Mixed	.....	209	104	45.5	23.0	0.9159
8	10 per cent No. 1 lard oil in mineral oil ..	Paraffin	10.12 lard oil	101	67	41	29.4	0.8794
9	5 per cent oleic acid in mineral oil	Paraffin	4.90 oleic acid	97	65	40.5	29.2	0.8805
10	Sulphurized mineral oil	Asphaltic	4.38 sulphur	105	67	40	21.6	0.9242
11	Sulphurized lard oil blended with 5 parts mineral oil	Mixed	2.34 sulphur 4.43 F.F.A. sulphurized 13.94 fat sulphurized	102	67	41.5	25.4	0.9018

No.	Composition	Temp., Deg. Fahr. Pour	Temp., Deg. Fahr. Flash	Temp., Deg. Fahr. Fire	N. P. A. Color[6]	C Specific Heat[2] 100 Deg. Fahr.	C Specific Heat[2] 210 Deg. Fahr.	C Specific Heat[2] 430 Deg. Fahr.	k Thermal Conductivity[3] 100 Deg. Fahr.	k Thermal Conductivity[3] 210 Deg. Fahr.	k Thermal Conductivity[3] 430 Deg. Fahr.
1	Dry cutting	.....	.....	...	.....	.....	.....	.....	.....	.....	.....
2	1½ per cent by weight of borax in water ..	.....	.....	...	.....	.....	.....	.....	.....	.....	.....
3	1 part soluble oil in 50 parts water	.....	.....	...	.....	.....	.....	.....	.....	.....	.....
4	1 part soluble oil in 10 parts water	.....	.....	...	.....	.....	.....	.....	.....	.....	.....
5	No. 1 lard oil	45	445	...	4	0.4510	0.5149	0.6438	0.8738	0.8448	0.7852
6	Light mineral oil	0 to —30	320–305	375	2–2¼	0.4500	0.5142	0.6430	0.8724	0.8440	0.7845
7	Heavy mineral oil	0 to —15	340–350	390	2¼–3, 3	0.4490	0.5137	0.6417	0.8695	0.8400	0.7818
8	10 per cent No. 1 lard oil in mineral oil ..	25	355	...	3	0.4630	0.5290	0.6612	0.9052	0.8750	0.8145
9	5 per cent oleic acid in mineral oil	25	295	...	3.5	0.4624	0.5284	0.6610	0.9048	0.8748	0.8138
10	Sulphurized mineral oil	0 to —25	285	...	Black	0.4459	0.5096	0.6374	0.8620	0.8344	0.7752
11	Sulphurized lard oil blended with 5 parts mineral oil	25 to 20	355	...	Black	0.4542	0.5190	0.6490	0.8837	0.8548	0.7942

[1]F.F.A. is free fatty acids.

[2]Specific heat C computed from formula $C = (t + 670)\ (2.10 - d)\ /2030$, in which t = temperature of fluid Deg. Fahr., and d = specific gravity of oil at 60 deg. fahr.

[3]Thermal conductivity k computed from formula $k = (0.813/d)\ [1 - 0.0003(t - 32)]$, in which d = specific gravity of the oil at 60 deg. Fahr., t = temperature of fluid in Deg. Fahr.; k is in units of B.t.u. per hr. sq. ft. per in. per Deg. Fahr.

[4]American Petroleum Institute.

[5]National Petroleum Association.

sults. Presumably the actual depth of cut for test No. 1 was slightly less than that for test No. 3, explaining why the curve for test No. 3 is above that of test No. 1. All three curves show practically the same general tendency as far as the influence of the various cutting fluids is concerned. In test No. 2, the dial reading for

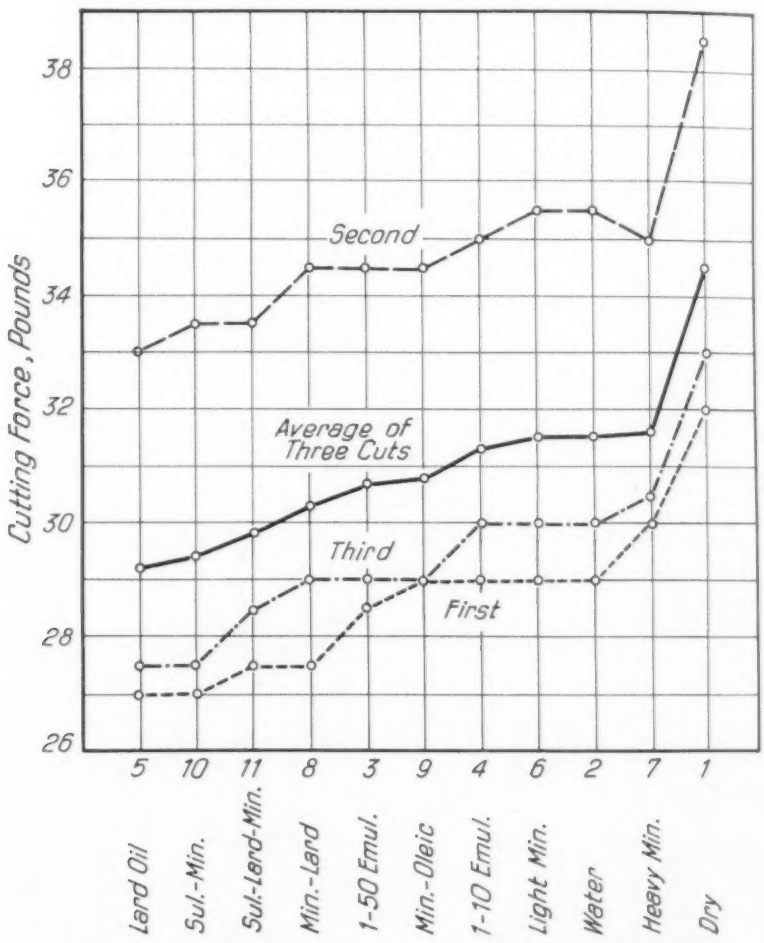


Fig. 6—Tangential Cutting Force in Turning Low Carbon Steel Using Various Cutting Fluids Shown in Table II. Cutting Fluids Arranged in Order of Increasing Cutting Force.

oil No. 7, a heavy mineral oil, is slightly low as compared with the curves for tests 1 and 2. The values for the three cuts have been averaged and are shown in Fig. 6 by the heavy dark line. The time required for these three series of tests, using the eleven cutting fluids, on the one material consumed a little more than three hours.

From the average curve, it is seen that the cutting fluids which show up most favorably in cutting this low carbon steel are the oils No. 5, 10, and 11. No. 5 is a lard oil, No. 10 is a sulphurized min-

eral oil, and No. 11 is a sulphurized lard oil blended with five parts of mineral oil. A gradual increase for cutting fluids No. 8 to 7 is seen, although the total increase is only 1 in 22. It is interesting to observe that cutting fluids No. 8, 9, 6, and 7 are oils, while No. 3, 4, and 2 are water compounds. Yet the difference in performance is not particularly noticeable. No. 1 at the extreme left represents

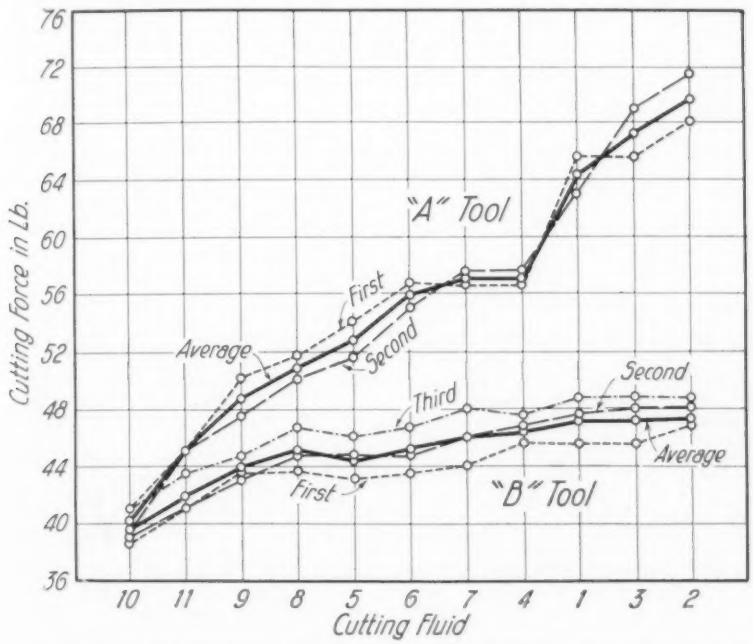


Fig. 7—Tangential Cutting Force in Turning Annealed S.A.E. 3150 Steel Using Various Cutting Fluids Shown in Table II. Cutting Fluids Arranged in Order of Increasing Force.

dry cutting. In all of the tests, the indicator readings when cutting dry are highest, as might be expected.

Cutting S.A.E. 3150 Steel Annealed—The influence of cutting fluids was further studied when cutting an annealed S.A.E. 3150 steel on which cutting fluid tests previously had been made by another method.[1] The results of the tests are shown in Fig. 7. Tests with two tools, A and B, were made for each of the eleven cutting fluids. Tool A, as described in Fig. 3, had 15-degree back rake and no side rake, while tool B was similar to A, except that it had 14-degree back rake and 8-degree side rake. The cutting speed was 66 feet per minute, the feed was 0.0069 inch, and the depth of cut was 0.10 inch. The stock was 1.808 inches in diameter at the start.

Two sets of tests were run with tool A and three sets with tool B using all cutting fluids in which the order of applying the cutting

fluids was varied. The results are shown plotted in Fig. 7. The heavy line for each tool represents the average of that series of tests. The cutting fluids are arranged as abscissa from left to right in order of increasing cutting force in pounds. The sulphurized oils No. 10 and 11 again produce the lowest cutting force. Oils No. 9 and 7, inclusive, show a gradual increase in cutting force from left to right as indicated. Cutting fluid No. 4, which is an emulsion consisting of one part soluble oil in ten parts water, produces the same cutting force as the heavy mineral oil, No. 7. Cutting fluids 1, 3, and 2, which are dry cutting, one part soluble oil in fifty parts of water, and water, respectively, show the highest cutting force for both tools.

It is interesting to note the difference in performance between tool A and tool B. The cutting force using the sulphurized mineral oil No. 10 is practically the same for both tools. All other cutting fluids, however, show distinctly different values of cutting force for the two tools, the difference increasing with the increasing cutting force. When using the heavy mineral oil No. 7, cutting tool A produces a cutting force of 57 pounds which is 24 per cent greater than that required by tool B, using the same cutting fluid. When cutting with water, tool A produces a force of 70 pounds which is 49 per cent greater than the force produced by tool B under this same condition.

In previous experiments[1] these same cutting fluids 10 and 11 were found to produce the lowest torque when drilling this same steel. The torque was found to increase with the cutting fluids arranged in the following order: 10, 11, 2, 3, 4, 7, 5, 6, 8, 1, 9. In planing, however, with a tool shape similar to that of tool B, but when taking a cut 0.2 inch deep and a feed of 0.036 inch, the cutting force was lowest for the sulphurized mineral oil No. 10, and was found to increase with the cutting fluids in the following order: 11, 5, 4, 8, 6, 7, 2, 3, 9, 1. In planing there seemed to be a very slight change in cutting pressure for the cutting fluids listed. When the planer force cut was 0.130 inch deep with a feed of 0.036 inch, the force increased with the cutting fluids in the following order: 10, 11, 2, 5, 3, 4, 7, 8, 1, 9, 6.

Investigating the Machining Qualities of Malleable Cast Iron

The machining qualities of a malleable cast iron will vary from

the surface into the body of the metal, due to the decarburizing effect of the annealing process. In structure, the material will vary from the surface to a depth of about 0.125 inch. This layer often is decarburized so that the metal at the surface consists of practically pure ferrite containing about 0.5 per cent of total carbon. The carbon content gradually increases until a normal value for the interior

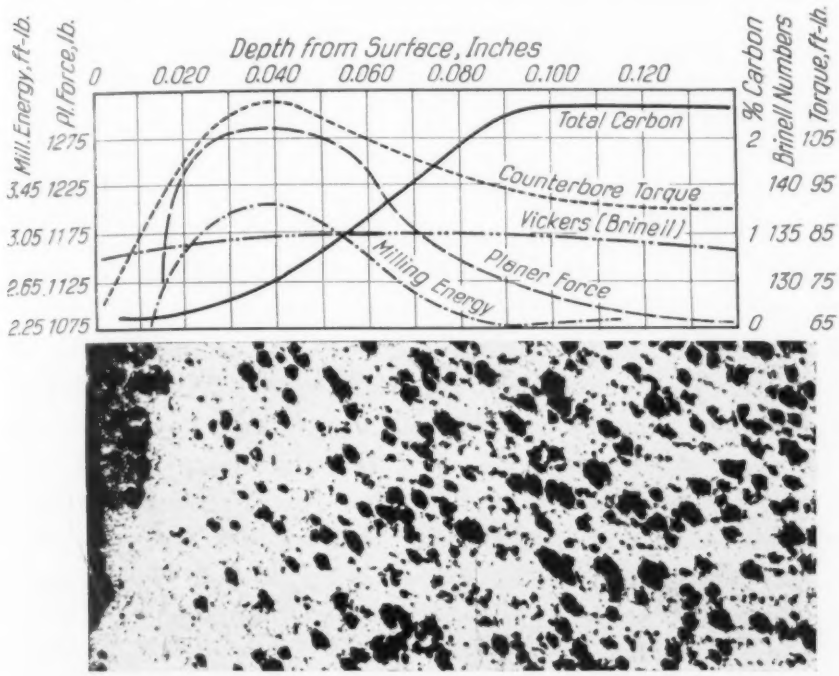


Fig. 8—Correlation of Machinability Values, Vickers Hardness Tests, and Per Cent Total Carbon of a Malleable Cast Iron Bar 1⅛ Inch Thick (Bar AA), and the Microstructure. The Outside Surface is at the Left. Etched with 4 Per Cent Picric Acid and 4 Per Cent Nitric Acid in Alcohol for from 5 to 10 Seconds.

is reached at the depth of approximately ⅛ inch from the surface. Perfectly malleableized iron will consist of temper or annealing carbon in a ferrite matrix throughout the body. In practice, however, this matrix may contain pearlitic areas, and usually carbide particles will be found in varying quantities. Often the surface layers to a depth of about 0.020 inch will be found to be spongy and oxidized in spots. The machining qualities depend on the distribution and relative quantities of these various constituents, the relative size of the grains, the presence of inclusions, sulphides, phosphides, etc., and will vary over quite wide ranges.

Fig. 8 illustrates such a structure magnified 14.3 times. The surface of the casting which was 1⅛ inch thick is at the left. The

analysis of the annealed iron taken from chips at a depth of 0.230 to 0.260 inch from the surface is as follows:

	Per Cent
Total carbon	2.32
Graphitic carbon	2.26
Combined carbon	0.06
Silicon	0.98
Manganese	0.293
Phosphorus	0.162
Sulphur	0.117

This bar was annealed in a periodic oven employing natural gas. It was packed in furnace slag and located in the center of the furnace. Medium tensile strength iron was anticipated. It required 44 hours to heat to 1600 degrees Fahr., and remained at or slightly above 1600 degrees Fahr. for 86 hours, with a mean cooling rate of 4.9 degrees per hour.

The curves over the photomicrographs show an attempt to correlate total carbon content as determined from layers 0.010 inch thick at various distances from the surface; hardness and machining properties at various depths is determined by the force on the planer tool as described in Fig. 5, the torque on a counterbore 2.5 inches in diameter, with a ¾ inch diameter pilot when rotating at 74 revolutions per minute and at a feed of 0.006 inch per revolution, and the energy absorbed by a milling cutter tooth in taking one chip at various depths when the depth of cut of each chip was 0.025 inch and the feed per chip was 0.010 inch. Satisfactory correlation between the three machining curves is seen to indicate the machining properties of the metal at any depth.

The object of this series of tests is to show the use of the tool dynamometer in determining these machining properties from the standard tensile test bars representing the heat. The eleven tensile bars used were cast from various heats in the same foundry, and represent commercial malleable irons. The particular bars used were selected from some fifty available specimens to give the widest range of chemical analyses. They are listed in Table III which gives for each bar the data of the pour, and the analysis of the hard iron, as determined from similar tensile test bars.

The procedure of the tests was as follows: The bars were first very carefully centered so as to run as true as possible in the lathe. Successive cuts each 0.010 inch depth were taken the length of the ⅝-inch diameter section with a feed of 0.0091 inch per revolution of

Table III

Malleable Cast Iron Tensile Test Bars, as Used in Tangential-Force Tests for Skin Variation. The test bars were selected from each of several pours of one company.

Bar No.	Date of Pour	Furnace No.	Hard Iron Analysis					Physical Properties		
			Silicon	Sulphur	Phos.	Man.	Total Carbon	Tensile Strength Lb./Sq.In.	Yield Lb./Sq.In.	Elongation in 2 Inches
1	2/16/31	1	0.98	0.041	0.17	0.29	2.35	55,000	37,000	22.5
2	2/17/31	1	0.84	0.047	0.19	0.29	2.37	55,000	37,200	22.5
3	3/4/31	1	1.05	0.043	0.17	0.24	2.43	54,800	37,200	23.5
4	3/18/31	1	1.14	0.040	0.17	0.23	2.47	55,000	39,000	20.5
5	3/23/31	1	0.93	0.042	0.18	0.22	2.29	55,000	34,000	27.0
6	4/15/31	2	1.18	0.048	0.18	0.24	2.01	59,500	39,700	29.2
7	4/22/31	2	1.05	0.040	0.18	0.22	2.14	56,000	35,400	28.0
8	5/ 6/31	2	0.96	0.043	0.18	0.24	2.20	58,500	37,400	25.8
9	5/18/31	1	0.86	0.036	0.18	0.23	2.45	57,000	33,600	23.5
10	5/25/31	1	0.86	0.044	0.19	0.24	2.50	54,700	36,300	23.0
11	6/ 8/31	1	0.88	0.047	0.18	0.26	2.12	61,000	37,600	23.0

the work. Readings were taken at three or four points during each cut and averaged. The tool bit was the "A" bit previously described.

In most cases, fifteen cuts were taken before the bars became so reduced in diameter that the deflection due to the cutting forces became excessive. The diameter of the bar after each cut was determined by the use of a micrometer, and the readings of the dial were corrected so they would correspond to the full size of cut described. The test data expressed as dial readings are shown graphically in Fig. 9, plotted over the distance from the surface to the center of the 0.010 inch depth of cut.

Bar No. 1 shows a typical machinability curve for malleable iron. The slight falling off of the curve at the surface is due mainly to surface irregularities rather than spongy iron. The peak occurs at about 0.020 inch, and the curve then falls uniformly to a minimum value at about 0.140 inch. It has been found, on rectangular test bars, that this minimum value occurs from 0.100 to 0.125 inch from the surface in most cases. It is believed that the cylindrical test bars used in this test decarburize to a greater depth.

Another typical curve is shown for bar No. 3 in Fig. 9. For bars 6 and 7 it is noticed the peak is much deeper in the metal, and the curve near the surface tends to flatten out. This indicates a much thicker band of nearly pure ferrite on the surface. The minimum points of the curves are also nearer the surface, indicating less diffusion of the carbon from the interior to the surface. The elongation in per cent in 2 inches shown for these bars in Table III is 29.2 and 28.0, respectively, and is the highest in the group, being much higher than usual for average malleable cast irons.

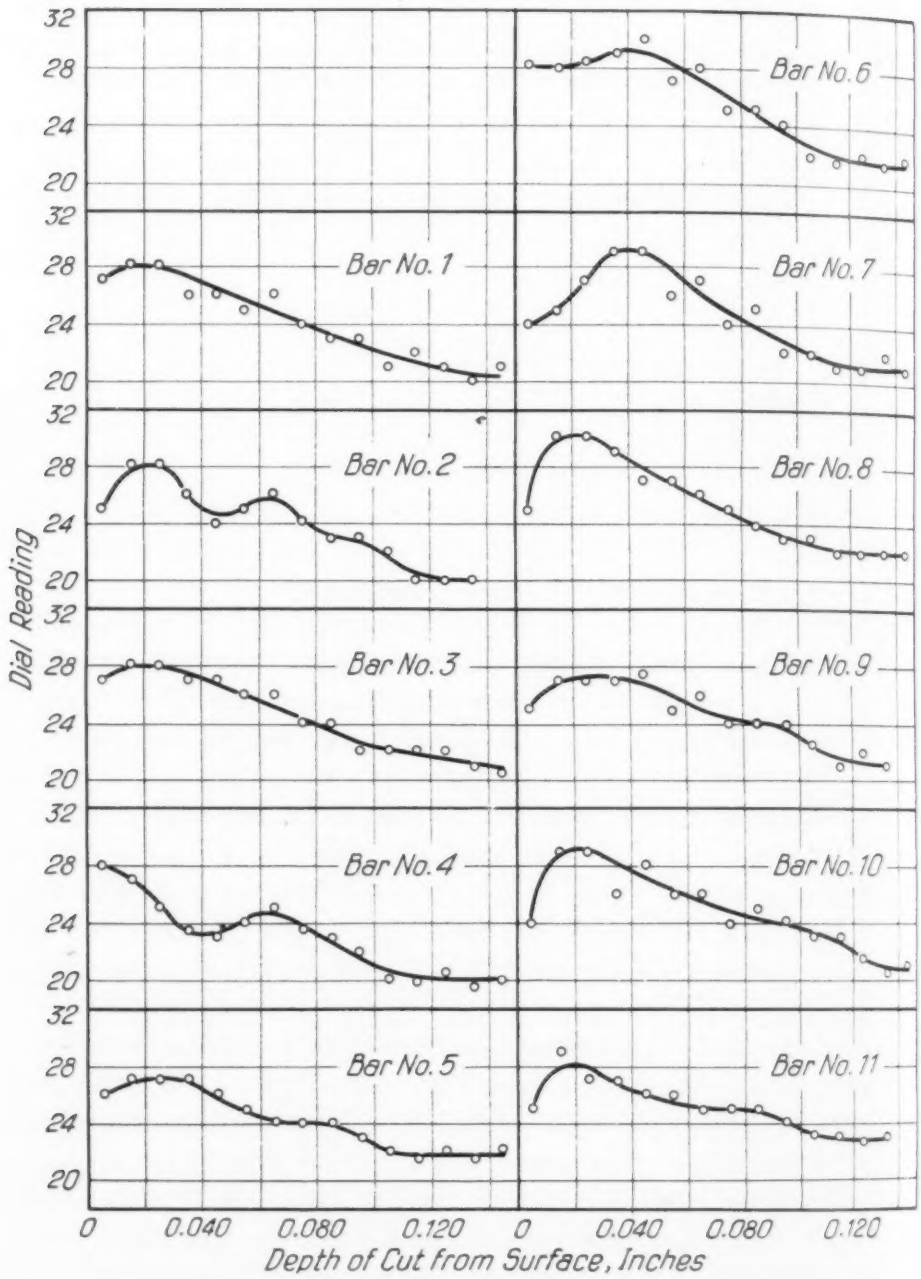


Fig. 9—Influence of Decarburized Skin on the Turning Properties of Malleable Cast Iron. Tool Dynamometer Dial Readings Obtained in Turning Malleable Cast Iron with Tool "A", Plotted Over Depth from Surface to the Center of the 0.010 Inch Depth of Cut.

A decided drop of the curve immediately at the surface, as for bars 2, 8, 10, and 11, usually indicates a layer of spongy oxidized iron, probably formed by absorption of furnace gases.

Humps in the curves are found for many of the bars, and are especially noticeable for bars 2 and 4. These humps invariably indicate incompletely malleableized iron, and examination under a microscope will reveal free carbides and pearlitic layers. Often specimens with less than 0.010 per cent of combined carbon in the interior matrix will show bands of nearly eutectoid composition near the surface and values of elongation are usually slightly lower than for correspondingly well malleabilized iron.

An interesting point to observe is that, although specimens were selected with total carbon contents ranging from 2.01 per cent for bar 6 to 2.5 per cent for bar 10, there seems to be no correlation possible between carbon content and physical properties or machinability. Machinability values seem to depend not so much on analysis as on structure and, in malleable iron, structure depends on the annealing cycle, type of packing, and furnace gases present quite as much as on analysis. It follows then that for similar irons, a simple machinability test of this kind will tell much about the iron and will indicate what changes, if any, might be made to improve the product or to reveal the effect of experimental changes in the annealing process.

Conclusions

In formulating conclusions of the experiments covered in this paper, it is necessary only to review briefly the results obtained.

1. The tool dynamometer has been found to work equally well in a lathe or shaper. It is a comparatively simple matter to determine an equation representing the cutting pressure as the function of the depth of cut and feed for a given speed and tool. The formula

$$P = 38{,}700\ F^{0.67}\ D^{0.94}$$

was found to represent this relation when turning the interior of a low carbon cold-finished steel. The formula

$$P = 155{,}000\ F^{0.78}\ D^{0.94}$$

was obtained when turning an annealed S.A.E. 3150 steel. The exponents of the feed and depth agree with those obtained in previous tests on a planer dynamometer.

2. Machinability ratings as determined by using the simple turning or shaping tests with the tool dynamometer described are

shown to agree remarkably well with machinability tests determined by milling, drilling, and planing for nine metals of different types, consisting of high carbon steel, medium carbon steel, free-cutting steel, manganese bronze, cast iron, cast aluminum alloy, bearing bronze, and an annealed screw stock brass. The amount of metal and the time required to determine the machinability ratings with the tool dynamometer are much less than are required for other methods of tests.

3. It is a simple matter to determine the influence of a cutting fluid when turning a given piece of material. The time and expense involved is very little indeed. When cutting a low carbon cold-rolled steel at 73 feet per minute with a depth of cut of 0.010 and a feed of 0.0091 inch, it was found that lard oil produced the lowest cutting force. Cutting fluids arranged in order of increased cutting force in pounds are as follows: lard oil, sulphurized mineral oil, sulphurized lard oil, mineral lard oil, 1 to 50 emulsion, mineral oil containing oleic acid, a 1 to 10 emulsion, a light mineral oil, borax water, heavy mineral oil, and dry cutting. The lowest cutting force produced was 29.2 pounds, with lard oil, whereas the largest cutting force with a liquid was 31.5 for the heavy mineral oil. Dry cutting shows a marked increase in cutting force to 34½ pounds.

A different arrangement of the same cutting fluids was found when arranged in order of increasing cutting force in pounds when turning an annealed S.A.E. 3150 steel. Furthermore, the influence of the cutting oils was shown to vary with the shape of the tool. A tool having a 15-degree front rake but no side rake produced a minimum cutting force of about 40 pounds with a sulphurized mineral oil, but a maximum force of 70 pounds when a borax water was used. All the other oils gave force values between these two points. When a turning tool having 14-degree side rake and 8-degree front rake was used, a minimum cutting force of 39.5 pounds was obtained with sulphurized mineral oil and a maximum of only 47 pounds was obtained when cutting with borax water. The order of the oils as they influence the cutting force when cutting the annealed S.A.E. 3150 steel is not the same as when the low carbon cold-rolled steel was cut.

4. The value of the tool for determining the cutting characteristics of the skin or decarburized layer of malleable cast iron was shown. In turning chips 0.010 inch depth successively from the

surface to the interior, the cutting resistance of the metal can be determined and shown graphically.

5. The authors feel that this simple and inexpensive tool can be used to advantage in determining absolute values when cutting under fixed conditions, or comparative values when a variable is introduced.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Theodore Thoren, who made some of the drawings, and Vasily Prianishnikoff, who ran many of the tests.

DISCUSSION

Written Discussion: By Alvan L. Davis, research engineer, Scovill Manufacturing Company, Waterbury, Connecticut.

For many years Professor O. W. Boston has been successfully putting salt on the tail of that elusive bird known as machinability. His contributions have placed all of us who are interested in this subject under obligation to him. The present paper is at once of established value due to the comparison that is made with results of his extensive earlier work, which affords the background and setting for the present paper.

The tool dynamometer described should make possible the more general testing of machinability by industrial consumers. The simplicity and relative cheapness of this new device, as well as its close agreement in results with the older laborious and costly methods of testing, should lead to its widespread use. One principal use will probably be the checking of stock for use on automatic screw machines, and investigation of cutting fluids used therewith.

An interesting fact brought out by this paper is the varying behavior of cutting fluids according to the stock being machined. Thus with the "A" tool, when turning S.A.E. 3150 steel annealed, No. 1 lard oil gives about 30 per cent greater cutting pressure on the tool than when using sulphurized mineral oil. This difference of 30 per cent agrees with the result of drilling tests by Boston and Oxford, on S.A.E. 3150 steel, where No. 1 lard oil gave 25 per cent greater net power consumption, than sulphurized oil. With the "B" tool, on S.A.E. 3150 steel, lard oil gives 11 per cent more cutting pressure than sulphurized mineral oil as compared with 11½ per cent greater pressure determined by Boston and Oxford for planer tests with these two cutting fluids. On the other hand, when cutting a low carbon steel, the "A" tool gives slightly less pressure with lard oil than with the sulphurized mineral oil.

Thus we have an illustration of the fact that, in machining operations, there is as yet no way of telling in advance just what cutting fluid will be best for any given job. It is still needful to "cut and try." The tool dynamometer should prove of value for this purpose.

Written Discussion: By A. L. DeLeeuw, Plainfield, N. J.

It is to be regretted that certain terms are used in the engineering prac-

tice which have no definite meaning or which may have a variety of meanings. Such a lack of definition leads to confusion and retards progress. One of these terms is the word "machinability." By some it is understood to mean the relative amount of power required for removing a certain amount of metal; by others the relative tool life; and by still others the ease with which a desired finish can be obtained.

The trouble with the three meanings which may be attached to the word "machinability" is that none of them stands entirely by itself. As an example, one kind of steel may require only a very small additional amount of power for the removal of metal as compared to some other kind, but the tool life on the first kind of steel may be very much shorter, so that it is possible to say that sample A is almost as machinable as sample B, and it is equally possible to say that it is very much less machinable.

Comparing wrought iron with some high grade steel, for instance, such as S.A.E. 3120, one would come to the conclusion that it is much more machinable; but if one tries to cut threads with a lathe tool or a die one finds that it is much less machinable, because in that case a certain excellence of finish is of prime importance. However, by changing the shape of the tool it is possible to produce a very excellent finish on wrought iron, but such a tool would not be practical for cutting threads on S.A.E. 3120. It may be said, then, with equal truth that it is not possible to compare the machinability of these two metals when the object is the cutting of threads. A similar condition comes up in the finished turning or milling or reaming of 45-point carbon heat treated steel with, say, S.A.E. 3120. It requires somewhat less power, tool life is about equal, but the finish is not so good.

Another thing to be regretted is that in the nature of the tests made, small depth of cut and light feeds are used. When taking a fine cut over 0.60 per cent carbon crucible steel, one obtains a good finish, the tool life is long, and the power required is about equal to that which is needed for lower grade steels; but when heavy cuts are used, the tool life is much shorter, there is a small but noticeable difference in power requirement, and the resulting surface is much torn up. When a cutting lubricant is used, we are confronted with a new set of conditions and when, in addition, we pay attention to cast iron, malleable iron, and the nonferrous metals, we get such a mass of confusing and contradictory evidence that the word "machinability" loses its meaning.

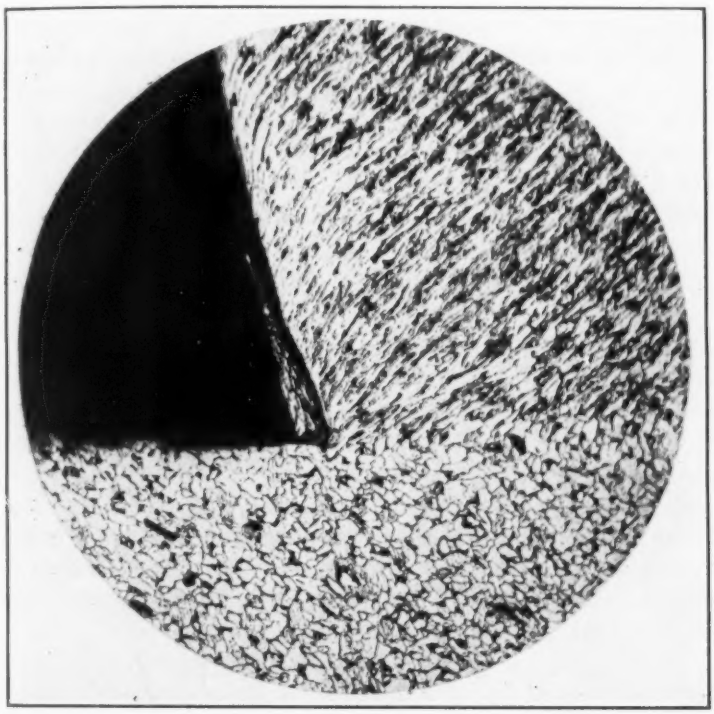
I have expressed myself a number of times at meetings of the American Society of Mechanical Engineers and in committee meetings as to the desirability of getting some fundamental knowledge of the cutting of metal. Until we start with these fundamentals, we cannot hope to co-ordinate the various ingenious and well thought out experiments which have been made from time to time, and to which Professor Boston has contributed so much. These experiments are of undoubted value, but they lack insofar as they do not point to principles upon which a complete structure can be built.

Written Discussion: By Hans Ernst, research engineer, Cincinnati Milling Machine & Cincinnati Grinders, Inc., Cincinnati.

The device proposed by the authors certainly provides a simple means for roughly determining the relative machinability of various work materials. As a scientific instrument it is open to the obvious objection that the results ob-

tained are affected by the exact shape and sharpness of the cutting edge, for which no criterion can well be established; but the close agreement between these results and the machinability ratings determined by other methods, proves its value as a means for quick comparison, and for routine tests of material for uniformity and ease of machining.

For routine testing against a predetermined standard, it will be necessary to provide proper gages or templates to check the shape of the tool bit after reconditioning. The deflection for a given load will also depend on the tightness of the screws which hold the longitudinal springs; thus, in practice, it



may be found more satisfactory to replace the present assembly of blocks and springs with a single tool steel holder, suitably heat treated, and milled or broached transversely to provide the required flexibility.

An interesting point in metal cutting which is again brought out by these tests is the general relation between tool pressure and feed and depth of cut. In the equation $P = C\ F^a D^b$, the exponent of D is always nearly unity, while the exponent of F is usually very much less than unity; thus showing that metal may be removed more efficiently by thick chips than by thin chips. This exponent also varies, from one test to another, over a much greater range than the exponent of D.

The reason for this relation is found by a study of the mechanism of chip flow. In the formation of a chip, the direction of crystal elongation, or material flow, is always substantially perpendicular to the face of the chip itself. This is clearly shown in the accompanying photomicrograph; crystal elongation being evident considerably in advance of the tool point. In the case of a

thick chip there is a less uniform distribution of stress through the chip section, and thus the average crystal deformation—and consequently the work done per unit volume—is less than in the case of the thin chip.

It is apparent that small differences in the physical structure of the work material even when of the same analysis, and small differences in the shape of the tool point, will cause considerable variation in the stress distribution through the chip section; thus the exponent of F will inevitably vary over a considerable range.

An important observation reported in this paper is the remarkable difference between the effect of various cutting fluids, when used with the tools designated as "A" and "B." For the tool "B" there was a relatively small difference in cutting force between the best and worst cutting fluids, while for the tool "A" there was a very great difference. It is evident that in the selection of cutting fluids we must carefully consider the exact shape of the tool itself. Apparently much additional work is necessary in this field before we can properly select the "best" cutting fluid for any particular job.

Written Discussion: By Dr. Ing. H. Schallbroch, Technische Hochschule, Aachen, Germany.

The design of a new and simple tool for measuring cutting force on a turning or shaping tool, developed by Professor Boston and Mr. Kraus, presents an interesting and ingenious method. It is true that it uses a maximum cutting depth of only 0.03 inch and a feed of 0.009 inch, giving a chip area of 0.00027 square inch, which is very small. In spite of the large shaft diameter (2.5 inches), in many cases there occurred a heavy "chatter," which would probably be further increased with the customary larger chip area.

Some time ago we performed experiments in Aachen with a similar apparatus, in which the turning tool deflected a steel membrane, this deflection being measured by means of a dial indicator. Even with a cutting depth of 0.08 inch and a feed of 0.008 inch the apparatus did not prove satisfactory.

The objectionable feature (as with all methods for measuring rapidly fluctuating forces by means of a purely mechanical indicator) was that for the necessary indicator range of, say, 50 divisions (1 division = 0.01 millimeter), the pointer could not follow with sufficient rapidity the fluctuations in force, thus making an accurate reading impossible.

Moreover, the unavoidable vibrations of the tool are already so great that a chatter occurs during the cutting process and the work does not proceed evenly. On the other hand, if a larger lever arm transmission is built connecting the indicator with the movable member of the mechanism to which the force is transmitted, the accuracy of reproduction of an indicator working within a certain tolerance (or within certain limits of accuracy) still cannot be improved; furthermore, the vibration of the needle will be increased.

We therefore built a cutting-force-meter (tool for measuring cutting force) (cutting force indicator) with a so-called "tragheitsfrei" (free from inertia or sluggishness) electrical enlargement device, which operated by transmission of the force from an elastic steel membrane. With this we were successful in obtaining without chatter not only large chip areas (for example, 0.10 square inch) but also high cutting speeds (240 to 300 feet per minute). Our experiences would seem to indicate that it is impossible to get reliable machin-

ability test results with mechanical indicators on the larger and very interesting chip areas (over about 0.003 square inch).

Setting aside these objections, we can agree that the authors have produced an instrument suitable for light cuts, with which a certain "relative machinability" can be determined in a short time and with small consumption of material. Here it must be emphasized that only through measurement of the cutting force resultant (measurement of the single components in the three main directions will not even suffice) can complete knowledge of the machinability of a material be obtained.

This supposition, however, is still not in accord with present-day experience, for in order to have complete data on machinability, we must know the tool life and the smoothness of the surface of the piece being tested, as well as the cutting force. Measurement of the cutting force does not give invariably accurate information on the last two points.

Furthermore, the suitability of a cutting fluid can be reliably determined by means of a simple cutting force measurement only when it has been proved that the tool life and the surface smoothness have a fixed relationship to the cutting force. It is possible in this case, as is the general practice, to draw conclusions about the important questions of tool life and surface smoothness from determination of the cutting temperature taken in combination with the force measurement.

The agreement between the cutting force measured by this new instrument and measured by other methods on a number of metals and cutting fluids, which is emphasized by the authors, should therefore not be interpreted as indicating a complete valuation of machinability; it indicates solely cutting force.

Nevertheless, this good agreement indicates that in spite of the difficulties described, Boston and Kraus have succeeded in developing a simple mechanical method for measuring cutting forces between about 12 and 65 pounds.

Written Discussion: By H. P. Croft, metallurgist, Chase Brass and Copper Co., Cleveland.

The authors have described a method for measuring pressures on cutting tools which is very simple in its construction, but should be quite valuable in comparing relative machinability of similar alloys. In order to investigate its use in measuring machinability of copper-zinc alloys, the writer produced a duplicate of this device. One slight change was made in this, which we consider beneficial, namely, a loose fitting tongue and groove connection between the shank and the tool bit holder which will prevent sideways thrust if using a tool bit with side rake. This fit is loose enough so that when well lubricated, the resulting friction should be negligible.

Due to lack of time, only a few tests were made, but these were sufficient to show that in machining free-cutting brass rod, the cutting forces plotted as functions of the feed and depth of cut, are similar in form to those shown in Fig. 2 of this paper. It was also found that the tool pressure is independent of the cutting speed in the range of 200-450 revolutions per minute, when machining a 1-inch rod. At 675 revolutions per minute excessive chatter was encountered.

Tests on several alloys show that the machinability, as measured by this method, is similar to that value as determined by other methods. We list be-

low the relative machinability, free turning brass rod being used as the standard of 100. These tests were made under the following conditions:

Diameter of rod	1 inch
Speeds, Revolutions Per Minute	200—300
Surface Speeds, feet per minute	52.5—78.5
Feeds, inch	0.009—0.063
Depth of Cut, inch	0.020—0.035

In the above table, we have included the average machinability as indicated by turning practice of several manufacturers and the average rating of these alloys for all types of machining, including drilling, chamfering, cutting off, turning, milling, sawing, and other operations. This last column represents averages of experimental work and actual practice, and has been gathered from a number of sources.

Alloy	Nominal Composition Copper	Lead	Tin	Machinability Rating Boston-Kraus Tool	Machinability Range from Drilling, Sawing and Chamfering Tests	Manufacturer's Turning Practice	Average Machinability
Free-Cutting Brass Rod, Drill Temper	62.00	3.50		100	100	100	100
Free-Cutting Brass Rod, Annealed Temper	62.00	3.50		95	90-100	100	
Leaded Commercial Bronze Rod	89.00	2.00		95	90-125		90
Brass Forging Rod	60.00	2.00		88	65- 93	90	80
Leaded Chamet Bronze Rod	60.00	.75	.75	78	60- 77	65	65
Chamet Bronze Rod	60.00	0	.75	50	30- 55	50	35
Corvic Bronze	98.50	0	1.50	29			25

Oral Discussion

A. HURTGEN.[1] It would seem that with such an amplifying device as the authors have presented for measuring tool pressures in lathe turning, that there would be such a considerable amount of vibration transmitted through the amplification arrangement that a definite indicator dial reading would be practically impossible, since in turning material not entirely uniform these variations would be amplified, with the result, that the indicator hand would be constantly shifting back and forth.

It also seems, that in commercial practice we are seldom permitted to put a piece of steel in that condition as will result in the least amount of tool pressure in machining, there being other limiting conditions which practically define within fairly close limits the physical condition of the material. We may be limited by certain physical properties of tensile strength, or ductility, or impact, or possibly, it is a matter of machine finish, or threading, which involve considerations quite independent of obtaining a measure simply of tool pressure.

We manufacture large numbers of forged valves and fittings for the oil refinery business wherein considerable pipe threading is involved as well as the turning of metallic gasket seat-rings both of which require a non-chatter finish. In this connection it has been found that the Brinell hardness most

[1]Metallurgist, Henry Vogt Machine Co., Louisville, Ky.

adaptable to threading is not the same as that most adaptable to good finish grooving, and the matter of machinability resolves itself into a consideration of a number of factors rather than a single proposition. If the material were permitted to be in the best condition for threading, or in the best condition for good finish turning, or in the best condition for a minimum tool pressure, each one entirely independent of the other, a simple test wherein the minimum tool pressure was determined would be very desirable from the standpoint of minimum tool pressure, but would be entirely without significance in ascertaining the condition best for threading, or the condition best suited for finish-turning. In this connection it is the writer's experience that very few parts can be considered which do not have at least several factors which must be considered from the standpoint of machinability, and that condition which lends itself most toward the machinability on one operation retards the machinability on another operation.

The writer is not convinced of the practicability of such a device in offering a means of securing accurate data which will be of particular significant service excepting for such operations where every consideration regarding the material will subordinate itself in order to obtain a certain tool pressure. Even then there is a question as to whether the excessive chatter transmitted through the amplification arrangement will permit a definite reading on the indicator dial.

I shall be very glad indeed to have the authors give me any enlightenment in the way of explaining how this test and the proposed device may be effectively and economically used for determining the best condition of a single part which is to be threaded as well as to contain non-chatter finish grooves, the threads, of course, being free from beards and of good finish, such as is required by the leading oil refineries in pipe line equipment.

Authors' Closure

Mr. DeLeeuw has raised some questions as to the meaning of the word machinability. This paper was not written for the purpose of discussing definitions of that term. The title of the original paper was changed from "A Simple Cutting Tool for Measuring Pressures in the Direction of Cut" to "Machinability Measured by a Simple Tool" for the preprinted abstract in *Metal Progress* of September, 1932. This over-emphasized the term machinability.

The term machinability covers several different things which, unless specifically stated, may lead to confusion. In the paper under discussion, it seems there can be little confusion as to the meaning of this term. It is used specifically in several different ways. One shows that the machinability ratings of several metals when tested by each of several different processes, such as planer tool force, drill torque, milling energy per chip, and drill penetration, give substantially the same results. The cutting tool in each type of test remains the same for each of the metals tested. Again, the cutting properties (as expressed by resistance to cutting) of a given steel are determined with a constant tool shape when several cutting fluids are used. These values are then again obtained when using a second form of tool, showing that machinability ratings, even as expressed in resistance to cutting, vary with the shape of the tool used.

Other methods of expressing machinability, such as by the life of a given type of tool when cutting these materials, were not involved in this paper. One may be interested in tool life, finish, cutting temperatures, cutting power, or any other property. A specific test for each purpose must be conducted.

The Society's Committee on Machinability of Steel, of which the author is chairman, is now preparing a definition of machinability and attempting to present pertinent data relative to this broad field. The Committee will appreciate comments and advice from any one interested.

The authors agree with Mr. DeLeeuw's closing remarks as to the desirability of obtaining fundamental knowledge of metal-cutting processes. The subject deserves united cooperation. The industries, however, apparently feel that such investigations are not worthy of their financial support and are leaving the matter largely to a few individual investigators. Until the fundamentals of metal cutting are known, no scientific basis for metal cutting can be laid down.

Mr. Ernst has made a suggestion which already had been carried out by the authors. The tool dynamometer as illustrated in the paper has been rebuilt, using a single piece of oil-hardening tool steel and machining an "H" from the solid piece so that the tool bit carrying end is attached to the shank by two springs consisting of the original bar. Tools of this type have been found to give absolutely straight calibration curves, representing the dial-gage deflections as a function of the load on the tool point. They were made slightly heavier than the tool discussed and so have given satisfactory results when cutting at higher speeds and when taking heavier cuts. These newer tools, just as the tool described in the paper, have been found to cut entirely satisfactorily, that is, without vibration, when moderate speeds and sizes of cuts were used. The capacity of each tool is found by observing that speed or that size of cut which causes the dial gage to start vibrating excessively. Until this capacity is reached, there is little trouble in obtaining duplicate observations. The accuracy which can be obtained with this tool, even when taking such light cuts, is shown by the close agreement between the formula for cutting pressure as determined by the simple tool and that of a large planer dynamometer on which cuts up to 10,000 pounds can be made.

The discussion by Dr. Schallbroch is very interesting indeed. The results of the similar experimental device built by him corresponds very favorably with the results obtained by the authors with their tool. It is appreciated that with this small tool only the resistance to cutting as measured in the direction of cut is obtained. It is also appreciated that the measurement of this cutting resistance may or may not have a bearing upon the general machinability of the metal as expressed by the finish of the cut surface or the cutting life of a given tool. As mentioned in Dr. Schallbroch's discussion, the tool was developed and has been used, it is believed, successfully, in comparing the machining properties of various materials. As pointed out in the paper, the tool is limited in the size of cut at which it will function properly and it also was pointed out that chatter occurred when the speeds were high. This is not considered as being objectionable for tests of these types. Such a tool is used principally for getting a hasty opinion as to the machining properties of various metals by removing only small amounts in a short time.

The results obtained by Mr. Croft with a tool constructed by him which is similar to that described in the paper are interesting indeed. The machinability ratings shown by the different methods in his table, are remarkably consistent. They are remarkably uniform, particularly when it is realized that the manufacturer's turning practice is based on tool life and that the second type of tests, based on machinability range from drilling, sawing, and chamfering tests, covers so wide a range of types of cutting. If such constant results can be obtained by the use of this small tool, it seems that the tool is very valuable indeed as a means of inspecting the quality of incoming material.

Mr. Hurtgen apparently does not accept the results of the experiments presented by the authors. It is true that the indicator of the dial gage did not remain stationary at a fixed deflection during a given test. Its motion, however, when the cuts were within the area of cut and cutting speed range, was confined to a range of a few thousandths of an inch on the dial gage. The range of vibration increases as the size of cut becomes large or the cutting speed becomes high. By a large cut or high cutting speed is meant that cut or cutting speed which causes excessive vibration of the dial gage needle and makes fairly accurate readings difficult. Not only did the tool described work successfully, but one built later for slightly heavier cuts worked even better because of the straight line calibration. Those made by Messrs. Croft and Schallbroch also seemed to give favorable results.

This tool dynamometer is not recommended as a "cure-all" to eliminate difficulties in machining a part by various processes. It is realized that the cutting pressure would not necessarily indicate the quality of finish which a material under a given condition might provide. That shape of tool could be found which would give a desirable finish when assisted by a suitable cutting fluid. The authors gave certain information obtained from experiments to show the influence that different cutting fluids have on the cutting force as determined by this simple tool. No information was given as to the influence of these cutting fluids on the finish produced, as it is felt that finish, like tool life, is quite independent of the cutting force, except possibly in a few specific cases. Just as Messrs. Ernst and Davis have summarized in their discussions, there appears to be as yet no way of telling in advance just what cutting fluid will be best for any given job without the cut and try preliminary test. Neither does there appear to be any single method of test which can be applied to determine the condition for best machinability for different processes or for different purposes of a given process, such as best tool life, surface finish, lowest power, etc.

The authors are grateful indeed to those who have contributed to the discussion of this paper, to raise questions, or confirm the practical use of the tool. While many types of tests and pieces of testing equipment are available for use in connection with machinability problems, the tool described was developed as a simple and quick means of throwing light on the subject of machinability, which has been found to be of value. The results with this tool appear to be of value only when they are directly comparative, showing simply that one material or one cutting fluid or one variable is better than another under the given conditions of the test.

DATA ON SOME SPECIAL STEELS FOR MACHINE GUN BARRELS

By V. V. deSveshnikoff

Abstract

Steels used in this investigation cover various promising alloy steels which were tested against the world war standard barrel steel, and the work was, of course, confined to those properties which might have a bearing on the service behavior of the gun barrels. Erosion (effect of sustained firing) and the accuracy of fire (registering the effect of this factor) tests were used and both microscopic and marcoscopic examinations of the fired barrels were made, and the findings correlated.

THE work herein described was begun about ten years ago under the counsel of Captain Fleming of the Ordnance Department, U. S. Army, and the late Dr. G. K. Burgess, Director, Bureau of Standards. The paper is an account of an investigation that was carried out at the Bureau of Standards with the cooperation of the Office of the Chief of Ordnance, U. S. Army. Other participants active in the work in other divisions of metallurgy were V. W. Bihlman,[1] A. L. Boegehold,[2] Sam Tour[3] and J. S. Vanick.[4] It is believed that the information herein contained may assist those desirous of continuing the study of the subject. These data also will give steel manufacturers added knowledge of the requirements for steels used for rifle and machine gun barrels.

The purpose of this investigation was to study the effects of the various metallurgical factors and the chemical compositions on the resistance of steel to erosion during gun firing. There is no generally accepted explanation as to what fundamental or characteristic properties the erosion resistance of steel is dependent upon.

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This paper is based upon data obtained in an investigation conducted at the Bureau of Standards and represents an abstract of an elaborate series of reports to the Ordnance Department, U. S. Army.

The author, Captain V. V. deSveshnikoff, is a consulting engineer, formerly associate metallurgist with U. S. Bureau of Standards, member of the Russian High Military Commission to U. S. A. in 1916. Manuscript received March 4, 1933.

Wear of a gun barrel consists essentially of the gradual enlargement of the bore until the rifling is destroyed and the projectile loses its velocity and proper speed of rotation and consequently its accuracy. Erosion to an oversized barrel is due to a combination of the wearing action of the bullet and the scouring blast of gases.

The investigation consisted of the manufacture and test of a number of barrels for the Browning machine gun from each of a series of steels practicable from the commercial aspect as well as being supposedly suitable for the particular purpose in view. These experimental barrels were fired to destruction under careful observation and an effort made to correlate characteristic physical properties of the steels with the behavior of the barrels during the firing.

The steels used in the investigation included various promising alloy steels which were tested against the World War standard barrel steel (high manganese-carbon).[5] The chemical compositions desired in certain cases involved definite modifications of certain of the chemical constituents one at a time so far as feasible for the purpose of determining the effect, if any, of the constituents in question.

Most of the steels were made by the crucible process, but several came out of commercial stocks. Each heat was cast into a 4-inch square ingot and rolled into a 1.5-inch round.

There is given in Table I a list of the various steels used, together with the identification number assigned to each steel. The heading at the top of each of the various classes into which the steels are grouped indicates the elements which were varied, the other elements being held, supposedly, constant.

Special Properties of Materials—The study of the properties of the chosen steels was naturally confined to those which, it seemed, might have a bearing on the service behavior of the barrels. Ease in forging, rolling and machining are fundamental requirements. Information relating to these properties, however, is gained by observation during the various necessary operations involved in the manufacture of the barrels rather than by special tests.

All carbon steels were treated to develop the following minimum requirements—a limit of proportionality of 75,000 pounds per inch when stressed in tension and an elongation of 20 per cent (2-inch gage length). These values were set as the minimum which any of the alloy steels would be expected to show.

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[5]Present standard machine gun barrel steel is: Carbon, 0.45-0.55; Mn 0.50-0.80; P 0.040; S 0.040; Si 0.10-0.35; Cr 0.40-0.60 per cent.

Table I
Chemical and Mechanical Properties of Steels Used

Heat No.	C	Mn	P	S	Si	Cr	V	Ni	Cu	Barrel No.	Heat Treatment Quenched in °F.		Tempered (a)		Tensile lbs./sq. in.	Prop. Limit lbs./sq. in.	Elongation in 2 in.	Reduction Per Cent	Brinell Hardness
Carbon-Manganese Group																			
4713	0.44	0.69	0.011	0.017	0.21					0	1600	Oil	900	N	124,650	75,000	20.0	45.5	241
1685	0.43	1.22	0.46	0.049	0.12					1	1500	Oil	1250	OF	114,650	85,000	23.0	58.5	244
1686	0.38	0.67	0.046	0.055	0.07					2	1600	Oil	950	N	112,800	70,000	20.0	45.5	228
1688	0.40	0.55	0.006	0.031	0.15		0.15			3	1575	Water	1200	OF	103,100	80,000	25.5	65.0	217
1689	0.55	0.92	0.020	0.026	0.26					4	1500	Oil	1250	OF	110,750	67,000	24.0	58.0	223
1702	0.22	0.075	0.008	0.028	0.02					10	1650	Water	500	OF	81,100	53,000	23.0	64.0	177
Chromium-Vanadium																			
1691	0.32	0.11	0.005	0.028	0.12	1.20	0.11			5	1600	Water	1200	OF	96,200	60,000	26.0	65.0	196
1692	0.27	0.44	0.005	0.031	0.09	0.69	0.14			6	1600	Water	1250	OF	95,100	73,000	26.0	69.0	196
Chromium-Vanadium-Nickel																			
1695	0.10	0.008	0.005	0.033	0.12	2.54	0.41	4.50		7	1650	Water	1175	OF	118,100	80,000	20.0	65.5	242
Low Nickel																			
1698	0.21	0.77	0.058	0.094	0.05			0.49		8	1550	Water	700	N	90,400	63,000	27.5	67.5	185
Chromium-Vanadium-Copper																			
1701	0.16	0.08	0.016	0.047	0.11	1.14	0.21		1.88	9	1650	Water	1300	OF	108,100	98,400	22.5	63.5	235
1729	0.32	0.28	0.017	0.046	0.15	0.80	0.28		2.76	15	1650	Water	1125	OF	107,450	70,000	24.0	66.0	241
Tungsten																			
1731	0.33	0.26	0.009	0.057	0.05			W3.82		16	1550	Water	1100	OF	94,500	70,000	28.0	61.0	241
1735	0.50	0.39	0.009	0.013	0.17			W1.59		19	1550	Water	1250	OF	104,850	90,000	28.5	56.0	248
High Chromium-Stainless																			
2040	0.25	0.40	0.006	0.010	0.77	13.98				20	1800	Oil	1250	OF	120,600	75,000	21.5	60.0	269
Manganese-Silicon-Chromium-Vanadium																			
1714	0.05	0.030	0.011	0.019	0.91	1.38	0.21			12	1750	Water	500	O	110,000	53,000	18.5	42.0	235
1725	0.35	1.45	0.012	0.056	0.20	1.11	0.13	Mo0.60		14	1625	Oil	1250	OF	115,600	100,000	22.5	58.0	241
1705	0.14	0.060	0.009	0.017	0.13	0.93	0.25			11	1650	Water	1325	OF	124,050	105,000	22.5	64.5	286
Manganese-Nickel-Silicon																			
1732	0.36	1.21	0.053	0.077	0.09			0.81		17	1525	Oil	900	N	113,500	90,000	24.0	53.5	225
1718	0.29	0.81	0.013	0.038	0.09			3.71		13	1475	Oil	1125	OF	112,300	92,000	25.5	65.5	235
1734	0.40	1.30	0.011	0.060	1.10			3.70		18	1600	Oil	1150	OF	142,500	65,000	26.5	45.5	277

(a) Tempering was done in oil (O), fused nitrate bath (N) or "Open Flame" (OF) as indicated.

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9C
12B
12C
13B
13C
16B
17B
17C
19B
19C
20B
20C

*No

Table II

Intensity of Erosion Cracking in the Different Barrels

Barrel No.	Number of cracks per unit length of arc of the bore Magnified × 50	× 100	Maximum Depth of Cracks mm	
1B	10 (6)*	75	1.15	
1C	15 (6)	69	1.53	
2B	20 (6)	46	2.45	Segregation
2C	25 (6)	38	1.25	
3B	17 (6)	71	1.60	
3C	25 (9)	93	1.60	
4B	24 (7)	45	1.46	
4C	26 (8)	48	1.09	
5B	24 (none)	37	0.76	
5C	32 (none)	49	0.62	
6B	40 (6)	90	1.30	
8B	27 (7)	45	2.19	
8C	68 (4)	110	3.22	
9B	30 (7)	59	1.00	
9C	17 (5)	37	0.85	
12B	22 (3)	22	1.16	
12C	13 (2)	39	0.93	
13B	56 (5)	96	1.24	
13C	30 (4)	84	0.85	
16B	16 (5)	46	2.91	
17B	40 (11)	133	1.60	
17C	29 (3)	100	1.12	
19B	33 (5)	70	1.40	
19C	25 (6)	67	1.69	
20B	28 (none)	67	0.69	
20C	37 (none)	61	0.62	

*Note Number of cracks exceeding 0.80 millimeters deep are reported in parentheses.

Mechanical Properties—The mechanical properties for the various steels of the chosen heat treatments are recorded in Table I. The barrel blank was treated prior to the boring and finishing operations. It was also found necessary, on account of machining difficulties experienced with stainless steel barrels, to heat treat the barrels from a "replacement" heat after the original barrel stock had been destroyed in drilling.

The barrel stock, received as 1.5-inch rod, was rolled into barrel blanks with the special barrel blank rolls at the Springfield Armory. Five full length blanks were obtained from each of the steels and also another blank a few inches short at the muzzle. All six of these blanks were heat treated at one time. The short barrel blank was used for chemical and physical test purposes, the other five being available for the manufacture of barrels. The barrels, when finished, were of standard design for Browning machine guns, and were made in the usual manner in the shops of the Springfield Armory, except that particular care was taken in the finish reaming and rifling to have the minimum permissible diameters between lands and grooves.

Firing Tests—Two tests were deemed to be necessary, i. e., the erosion test and an accuracy of fire test. The objective was to

correlate the results of these tests with the properties of the steels.

The erosion test was intended to determine the effect of sustained firing upon the rifling of the gun. Observations upon pressure, velocity, barrel temperatures and physical dimensions were included as part of the program. Continuous fire was interrupted periodically to measure the rifling, etc., after cooling and cleaning. All barrels were star-gaged and plug-gaged at the beginning and after each 2000 rounds up to 6000 rounds and thereafter after each 1000 rounds. Wax casts of the chamber were taken after every 2000 rounds up to 6000 rounds; then after every 1000 rounds. At the completion of the test the barrels were sawed open lengthwise and photographed. Wax casts were also photographed for purposes of record. Velocities were determined by taking the mean of ten shots from each barrel at the beginning, after every 2000 rounds up to 6000 rounds, then after every 1000 rounds. The taking of velocities was discontinued after 10,000 rounds. Temperatures were taken 8 inches from the bullet seat toward the muzzle after every 2000 rounds.

The accuracy of fire test was expected to register the effects of erosion upon this factor. Efforts to approximate extreme conditions required that there be no stoppages for cooling or cleaning. Therefore, 3 to 5 targets of 50 shots each were taken from a screen 100 feet from the muzzle, while the gun was hot and firing automatically at the maximum rate for sustained firing. Vertical and horizontal dimensions of the shot groups on each target were measured at the beginning of the test and then after the finish of every 2000 rounds up to 6000 rounds and subsequently upon the close of every 1000 rounds until the shot groove dimensions were considered too great. All firing was done from the Model 1918 tripod mounted on a T-base and held by sand bags. All barrels were finally fired 11,000 rounds regardless of the limit of their accuracy life.

Macroscopic Examination of Fired Barrels—A study of the macrostructure of the split barrels, after firing, was made at the Bureau of Standards for the purpose of determining the physical homogeneity of the various steels and the degree of "fiberization". The investigation as a whole, however, has confirmed the assumption made here, that the firing influences the surface metal only, so that the macrostructure of these fired barrels is identical with that of the initial stock. The examination indicated, as might be expected, that the barrels forged from the special heats, which were relatively small (100 pounds) as compared with the regular ingots used for machine

gun barrel stock (5000 pounds), showed that the original dendritic (ingot) structural pattern had not been entirely replaced by "fiberization" by the working of the steel from the ingot into the 1.5-inch round stock. Chromium-vanadium, stainless and standard steels (Barrels No. 5, 20 and 1) were not made special, but were worked down as customary in usual steel practice. The advanced position in terms of "accuracy life in rounds" in which these steels finished demonstrates the importance of the "working down" factor in the steel mill and is confirmed by the macrostructural characteristics.

The results cannot be summarized in graphical or numerical form. A secondary but important feature is the characteristic surface cracking of the bore surface which results upon firing. The predominance of rather long prominent cracks extending in a longitudinal, spiral direction in the grooves and of numerous short parallel transverse cracks on the "lands" are apparently related to, if not entirely determined by, the tracks of cutting tool edges left in the surface after machining these two different parts of the bore.

Microscopic Examination of Fired Barrels—In addition to the macroscopic examination of sections of the fired barrels for the determination of the structural and chemical changes which occur in the surface metal along the bore of the gun, a study was made by means of the microscope of the intensity and distribution of the surface cracking. This was carried out on 28 barrels which had been fired under similar conditions to a total of 11,000 rounds in each case.

The point at which the attack is most severe lies approximately 0.6 inch from the origin of the rifling.[6] The number and depth of the "erosion" cracks vary with the character of the steel. In Table II are summarized the results obtained in the examination.

Table III gives the average accuracy records of the various barrels after being fired 2000, 4000, 6000, 7000 and 8000 rounds.

In comparing the accuracy targets for the different barrels after the same amount of service, the degree of "clustering" of the shots was used as the criterion in making the arrangement rather than the method ordinarily used for expressing "accuracy" in such cases. In Table IV is given the order in which the various targets stand for each series (B and C) after 6000, 7000 and 8000 rounds.

In Table V is given the velocity records of the barrels reported upon by the Springfield Armory. The loss in velocity, as based upon

[6] V. V. deSveshnikoff, "Some Factors Affecting the Life of the Machine Gun Barrels," TECHNICAL PUBLICATIONS, No. 191, Bureau of Standards, p. 18.

Table III

Accuracy of Fire Tests—Springfield Armory Data

Arrangement of Barrels in Order of Accuracy. Number 1 in List Being the Smallest Area Covered by the Shots

Order No.	2000 Rounds		4000 Rounds		6000 Rounds		7000 Rounds		8000 Rounds	
	B Series Barrel*	C Series Barrel*	B Series Barrel*	C Series Barrel*	B Series Barrel*	C Series Barrel*	B Series Barrel*	C Series Barrel*	B Series Barrel*	C Series Barrel*
1	2 (11.3)	3 (10.7)	2 (10.4)	1 (6.9)	19 (13.7)	2 (12.4)	20 (32.5)	5 (17.0)	(Not rated)	17 (40.1)
2	8 (11.5)	17 (11.3)	12 (12.0)	4 (9.4)	9 (20.6)	20 (15.9)		19 (23.7)		20 (43.5)
3	19 (12.7)	2 (11.8)	5 (13.4)	2 (10.7)	17 (25.3)	4 (16.1)		17 (28.5)		
4	4 (13.6)	5 (14.1)	6 (13.6)	5 (11.5)	12 (26.0)	19 (16.9)		20 (36.2)		
5	3 (14.0)	4 (14.2)	19 (13.9)	3 (13.4)	5 (29.6)	17 (18.1)		3 (54.2)		
6	17 (15.6)	12 (14.9)	9 (15.8)	9 (14.1)	6 (48.4)	5 (18.4)				
7	1 (16.8)	13 (14.9)	4 (18.6)	20 (14.1)	13 (55.4)	1 (18.5)				
8	5 (17.6)	1 (15.3)	17 (20.9)	12 (17.3)	20 (87.5)	9 (19.0)				
9	13 (19.1)	9 (16.3)	3 (24.0)	17 (20.3)	8 (145.9)	12 (21.7)				
10	12 (19.5)	8 (16.5)	8 (25.4)	19 (20.3)	16 (192.2)	3 (23.6)				
11	9 (21.1)	19 (17.0)	13 (26.1)	13 (27.7)	(1) a	13 (35.4)				
12	6 (23.1)	20 (21.3)	*1 (48.8)	8 (34.6)	(2) a	8 (86.7)				
13	20 (28.8)		16 (55.2)		(3) a					
14	16 (35.2)		20 (94.9)		(4) a					

(a) Not rated. (*) Accuracy as determined by area of ellipse in the usual way.

Table IV

Accuracy Targets Arranged in order of Efficiency

Order	6000 rounds Barrel No.	7000 rounds Barrel No.	8000 rounds Barrel No.	9000 rounds Barrel No.
1	2C	19C	17C	20C
2	19C	5C	20C	
3	19B	17C	5C	
4	3C	20C	3C	
5	9B	3C		
6	12C	9C		
7	17C	20B		
8	1C	13B		
9	4C	12C		
10	9C	17B		
11	5C	4C		
12	5B	5B		
13	20C	9B		
14	17B	19B		
15	13B	2C		
16	13C	1B		
17	20B			
18	6B			
19	4B			
20	8C			
21	16B			
22	2B			
23	12B			
24	3B			
25	8B			

the initial value, that is, velocity at the beginning of the test, rather than the actual velocities, is given as an aid in comparing the different records. Measurements of the barrels in various stages of erosion (star-gage measurements) were charted graphically. The diameter measured on the lands and grooves was plotted along the length of the barrel. The normal wear of the bore surface, when plotted, results in a line of fairly uniform slope from the muzzle end, where the wear is least (ordinarily), to the breech end where the erosion is greatest. The progressive wear of the barrel after firing results in a family of curves of the same general shape, placed one above the other. Without exception, the wear on the lands is much greater, as might be predicted, than in the grooves of the same barrel.[7] The area under each of the curves was measured by means of a planimeter, thus giving a measure of the volume "wear" of the different barrels fired for the same number of rounds as well as the progressive "wear" for any particular barrel during its life. Aside from giving a general idea of the dimensional change of the bore at the breech and the muzzle end, the measurements do not appear to yield information of any value. They are not reported here.

[7] See TECHNICAL PUBLICATION, No. 191, Bureau of Standards, p. 8.

Table V
Per Cent Decrease in Velocity After Firing

Order No.*	Barrel No.	Velocity at beginning	Decrease after 2000	Decrease after 4000	Decrease after 6000	Decrease after 7000
1	20B	2632.0	1.14	2.26	3.18	3.99
2	13B	2605.8	0.28	1.07	2.10	4.02
3	5B	2612.0	0.69	1.15	2.75	4.06
4	19B	2609.0	0.53	2.33	2.53	4.10
5	3B	2655.5	2.01	2.84	3.14	4.72
6	17B	2612.0	0.54	2.18	3.95	5.02
7	6B	2623.0	0.57	2.49	3.16	5.45
8	16B	2620.0	0.68	1.53	2.71	6.91
9	12B	2601.2	0.38	0.67	1.97	6.97
10	4B	2618.8	0.79	1.32	2.95	7.59
11	8B	2635.6	0.48	1.43	3.32	7.65
12	9B	2668.5	0.36	2.98	5.19	7.81
13	2B	2654.3	1.41	2.42	5.06	7.84
14	1B	2618.0	0.61	1.39	4.04	8.09
1	5C	2629.0	0.88	1.70	2.62	4.18
2	4C	2616.2	0.31	2.64	3.60	4.40
3	17C	2622.8	0.56	2.49	3.00	4.61
4	13C	2613.0	0.37	1.24	1.64	5.74
5	19C	2640.0	1.44	1.89	2.65	6.05
6	9C	2665.1	2.07	2.78	4.62	6.16
7	1C	2622.0	0.88	1.02	3.05	6.79
8	12C	2660.0	2.26	2.63	3.31	6.88
9	2C	2640.0	1.17	1.89	3.30	7.12
10	3C	2644.8	0.93	1.77	4.34	7.49
11	20C	2643.0	1.48	2.72	5.15	7.83
12	8C	2665.2	2.00	3.65	4.70	8.18

*Arrangement based on decrease in velocity after 7000 rounds.

Results of Investigation

The scope of the investigation changed considerably during the progress of the work. Many of the changes were unavoidable. However, two main purposes were in mind when the investigation was instituted and the various tests were planned accordingly. These were, first, to find a steel having erosion resisting properties when used for machine gun barrel construction superior to those of the steels which were used for this purpose by the U. S. Army; second, to determine upon what fundamental characteristic properties of a steel "erosion resistance" depends. Although the investigation has not given results which will permit complete answers to the questions which started it, the results obtained are of considerable value and interest in adding to our previous knowledge of the life of the machine gun barrels. It is evident from the results obtained that there are notable differences in behavior of the different barrels.

In ranking the barrels with respect to erosion, it is most convenient to compare them with the standard at that time, barrel No. 1. Of the barrels tested, No. 20, 17, 5 and 3 were superior to the "No. 1

barrel", the first three being distinctly so. They all showed less wear on the lands and grooves at the breech section of the bore. For many of the others, including barrel No. 1, the rifling was completely worn away for a distance of several inches at the breech and with a considerably smaller number of rounds fired. In accuracy, all the barrels listed above surpassed barrel No. 1, the comparison being based upon the condition of the targets. The depth of penetration of the erosion cracks was also considerably less in most cases and the decrease in velocity noticeably less.

It is evident from the tests that superiority of the different steels over barrel No. 1 is associated with the differences in composition; namely, stainless and manganese-nickel steel, are the outstanding performers followed by chromium-vanadium types. Of these, No. 20, 5 and 3 are commercial steels worked down from large ingots which undoubtedly influenced their favorable performance.

Of these four steels, the stainless steel (No. 20) was the best in the lot. The chromium-vanadium and carbon-vanadium steels closely approximate commercial compositions. The nickel-manganese composition is commonly made into castings, but its unusually good record in wrought form for gun barrel service is noteworthy. The tensile properties were of little value as a performance index as they exceeded the usual minimum physical requirements.

A feature observed in the barrels listed as giving superior results which may be of some significance, or at least is believed to be worthy of consideration, relates to the behavior of the steels upon heating, as recorded in the expansion curves. Steels No. 20, 17, 3 and 5 are of the type in which the cooling or "down" curve is either coincident with the heating or "up" curve or close to it for equal cooling rates, thus indicating small, if any, permanent dimensional changes resulting from the transformation in the steel. All of the steels which showed a relatively wide gap (permanent dimensional change) between the "up" and "down" curves in the expansion measurements gave inferior results in the firing tests. Certain steels were eliminated without finishing their firing schedules because the barrels became swollen or bulged while hot, during firing.

The disqualifying of a gun due to a bulging barrel or similar cause appears to be more closely related to the mechanical properties of the steel at low and elevated temperatures than is the erosion resistance. Although bulging was not encountered in all the steels having the lower tensile properties, the cases which did occur were

confined, for the greater part, to such steels, mostly low carbon types.

An attempt was made to correlate the temperature observations made on the barrels while still hot from firing with the progressive "wear" record obtained by means of the star-gage measurements, but without any degree of success. It is of interest to note, however, that at times temperatures considerably above the average were obtained for some of the barrels listed as superior. Thus the temperature of barrel No. 3 was at one stage reported as 1650 degrees Fahr. and later 1380 degrees Fahr., while barrel No. 1 reached 1150 degrees Fahr. at one time and barrel No. 20, 1025 degrees Fahr. Even in cases of exceptionally high temperature observations, 2000 degrees Fahr. or more (barrels No. 9B, 12B, 13B), nothing exceptional or striking was found upon gaging.

A commercial stainless steel of the 14 per cent chromium type showed least erosion and greatest accuracy. An experimental manganese-nickel steel containing about 1.25 per cent manganese, 1 per cent nickel and rather high in sulphur (0.077 per cent) led the remaining low alloy types and indicated possibilities in its development for machine gun services. Warehouse grades of chromium-vanadium and carbon-vanadium steels came next in line and emphasized the importance of commercial processing since (with the stainless steel mentioned above) they were the only steels rolled into bars from mill-sized ingots.

Expansivity versus temperature curves suggest that steels, which upon cooling retrace the course of their heating curves, producing the smallest dimensional changes in passing through the thermal transformations, demonstrate superior performance in the firing tests.

Mechanical properties where merely set to acceptability under the prevailing barrel steel specifications failed to disclose any important relation between the life of the barrel and the different steels. It is probable that the raising of the tensile strengths to higher levels in those steels which could afford to sacrifice some ductility would improve their service. Bulged barrels or overstressed barrels occurred only in the weaker, lower carbon steels when heated rather hot by sustained firing, indicating the importance of elevated temperature strength of at least the short time test type.

A MICROSCOPIC STUDY OF STEEL WITH POLARIZED LIGHT

By Yap, Chu-Phay

Abstract

This paper describes some photomicrographic studies made by the use of polarized light. The purpose of the present investigation was to study the value of a polarizing microscope in revealing the structural phases in quenched and tempered steels in the light of present day knowledge obtained by other methods. The method of preparation of the specimens is discussed. The results obtained are reviewed in detail.

ALTHOUGH the polarizing microscope has been extensively used in mineralogical studies of thin sections, its adaptation to the reflection method of study of opaque samples has been less general, as the underlying theory is not so well understood. The pioneer work on the effects of polarized light on opaque minerals is due to Koenigsberger,(1)* Wright,(2) Schneiderholn,(3) Osborne,(4) Fairbanks(5) and Sampson(6). The most recent improvements in the technique of examining opaque minerals must be attributed to Sampson, according to Short(7).

The use of polarized light in the study of alloy structures was, insofar as the writer is aware, first suggested by Hanemann(8). Heindlhofer and Bain(9) evidently made some preliminary examinations of quenched steel. Recently, Primrose(10) and von Schwarz(11) made use of the polarizing microscope in a metallographic study of nonferrous metals. No systematic study of steel has ever been undertaken. In order to answer the question "what does a polarizing microscope reveal regarding the structural phases in quenched and tempered steels, in the light our present day knowledge obtained by other methods of investigations?", the writer undertook a systematic study of the problem. In spite of the tre-

Facilities for this investigation were provided the writer by the Department of Chemistry, Washington Square College, New York University, through the kindness of Prof. William F. Ehret.

*The figures appearing in parentheses pertain to the references appended to paper.

The author, Yap, Chu-Phay, is a member of the society. He is associated with the Research Institute of Physics and Chemistry, Directorate of Ordnance, Ministry of Military Administration, Nanking, China. Manuscript received March 18, 1933.

mendous amount of work on the structural phases in quenched steels and the behavior of the phases with respect to thermal treatment, no general agreement prevails. As will be shown, the evidence obtained with polarized light, when properly correlated, will be of some value in aiding us to clarify some of the controversial points.

As Short(7) gives the complete details regarding various methods of using polarized light in the study of opaque substances, we shall discuss here only the more fundamental points involved. Opaque minerals and metals belonging to the isometric system are naturally isotropic when examined with polarized light, while a polished section of an anisotropic substance will show a change of color or change of intensity of light during a 360-degree revolution in rotating the stage of the microscope. Some minerals show four extinctions during the revolution, thus behaving like anisotropic transparent substances when examined in polarized light by transmission. The cause of this phenomenon is not well understood, although Sampson(6) properly suggests that it is due to light absorption being different in certain directions from others, i.e., it is analogous to pleochroism in a transparent mineral. The usual case is that only two extinctions are observed. In a rotation of the stage, the mineral sample first rotates the plane of polarization to the right up to a rotation of 90 degrees when the plane of polarization will be rotated to the left, i.e., in a complete rotation of the stage there are two rotations to the right and two to the left.

There are three ways of detecting anisotropism as discussed by Sampson(6), first, with the analyzer in the crossed position; second, with the analyzer slightly rotated from the crossed position and third, by the use of the Wright biquartz wedge and nicol. Short claims the first method is the least sensitive, although in the case of steels the writer discovered that by the use of a cobalt-blue glass as a light filter, the change in the light intensities becomes sharp whether the nicols are completely crossed or not. In the apparatus used by the writer—a Reichert (Austrian-made), with a special attachment for the polarizer and the vertical illuminator—the analyzer is fixed but the polarizer can be rotated. In general, however, it is best not to cross the nicols completely, especially when photomicrographs are being taken.

The amount of rotation produced by an anisotropic mineral ranges from zero to a maximum (depending on the direction of the

polished section with reference to the orientation of the particular mineral under observation), which is a characteristic of the mineral. The measurement of the maximum angle of rotation in polished section is attended with such great difficulties as to make it practically worthless. The writer has availed himself of the monograph by Short in giving the details of the method, because the clarity of his presentation could not be improved on. Anyone wishing to undertake the study of alloy structures by means of polarized light is urged to study this monograph.

Two steels, containing 0.8 and 1.2 per cent carbon, were used; the former was quenched in water from about 1200 degrees Cent. (2190 degrees Fahr.), while the latter was quenched in oil from 1100 degrees Cent. (2010 degrees Fahr.). The quenched samples were polished with the least amount of cold working, as well as surface tempering. In all cases of repolishing, the samples were reground on 00 French emery paper, as ordinary wet-cloth polishing merely produced a thin, apparently amorphous surface without completely removing the previous polished surface which had been altered by the action of the acid etchant. Thus, in a steel in which Fe_3C is already precipitated in colloidal dispersion, the acid etchant not only removes the apparently amorphous surface, but also attacks the colloidal Fe_3C forming complex hydrocarbons. Hence, repeated etching should be avoided. It was likewise found after considerable trial that a very light etching with a solution of one per cent nital (HNO_3 in alcohol) is the best method of removing the superficial film without unduly altering the true structural features of the samples. Also a very light etch can be much more easily controlled, so that maximum contrast may, therefore, be obtained.

The reason an 0.8 per cent carbon steel was used is that it gives on quenching a structureless martensite or hardenite, and is therefore an interesting structure to study.

I. *α–Martensite*—Although in ordinary light, the structure appears homogeneous, in crossed nicols, however, it is observed to be highly anisotropic as shown in Figs. 1 to 4. It apppears that when a steel is quenched from a high temperature, the coarse-grained austenite (due to grain growth at high temperatures) is transformed in "blocks" to α–martensite, another solid solution. In the writer's opinion, Heindlhofer's and Bain's observation(9) that α–martensite is coarse-grained is correct, although it is somewhat doubtful if the

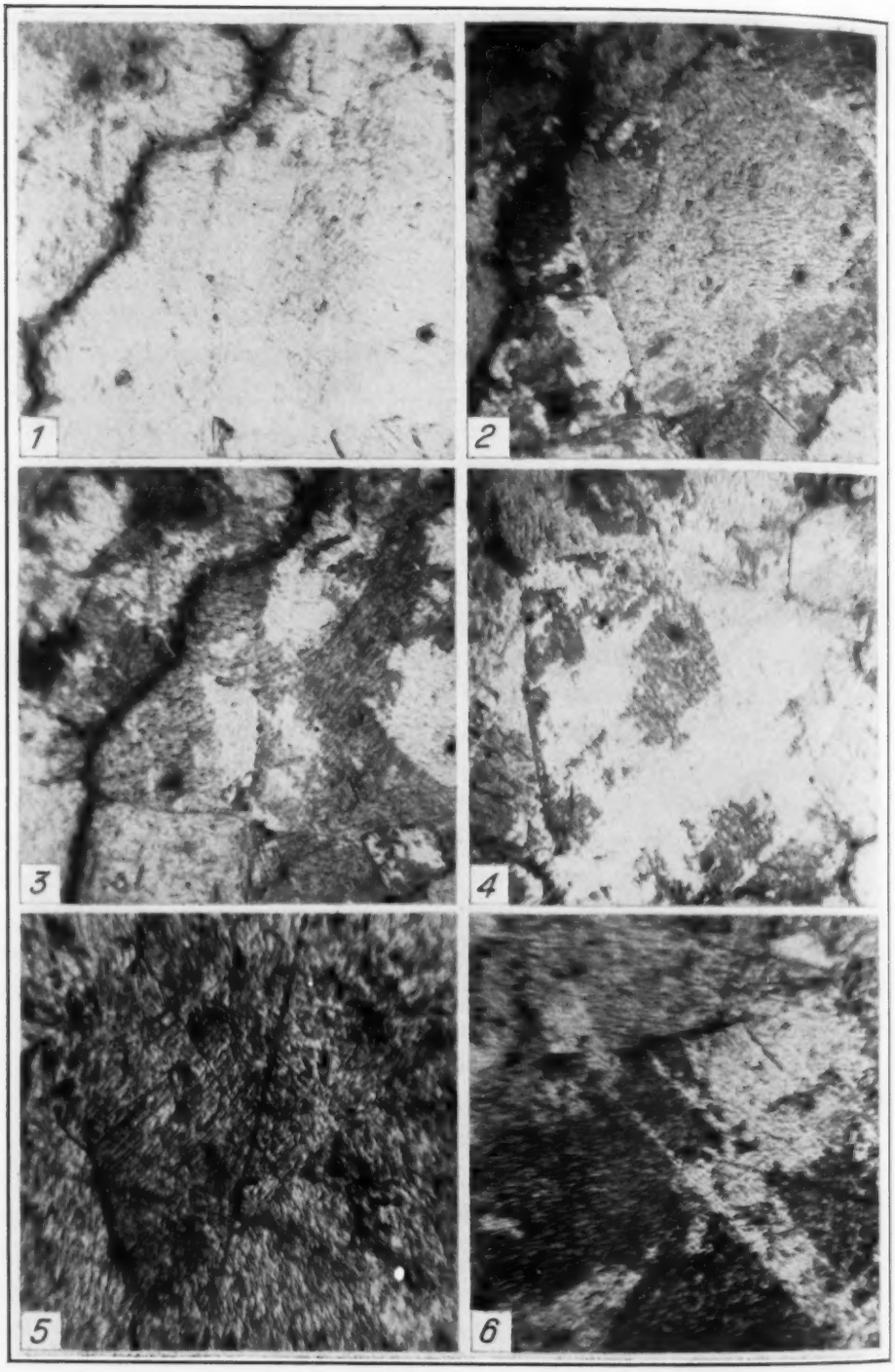


Fig. 1—Structure of α-Martensite 0.8 Per Cent Carbon Steel in Polarized Light Rotated in the Position of Maximum Extinction of an Apparently Large Grain.

Fig. 2—Same as Fig. 1 but in Ordinary Parallel Light; Note Absence of Structure.

Fig. 3—Same as Fig. 1 in Crossed Nicols and Rotated a Few Degrees. Grain is Really Composed of Several Units.

Fig. 4—Same as Fig. 1 in Crossed Nicols and Rotated a Few More Degrees. Units Which Were Dark Are Now White, and Vice Versa.

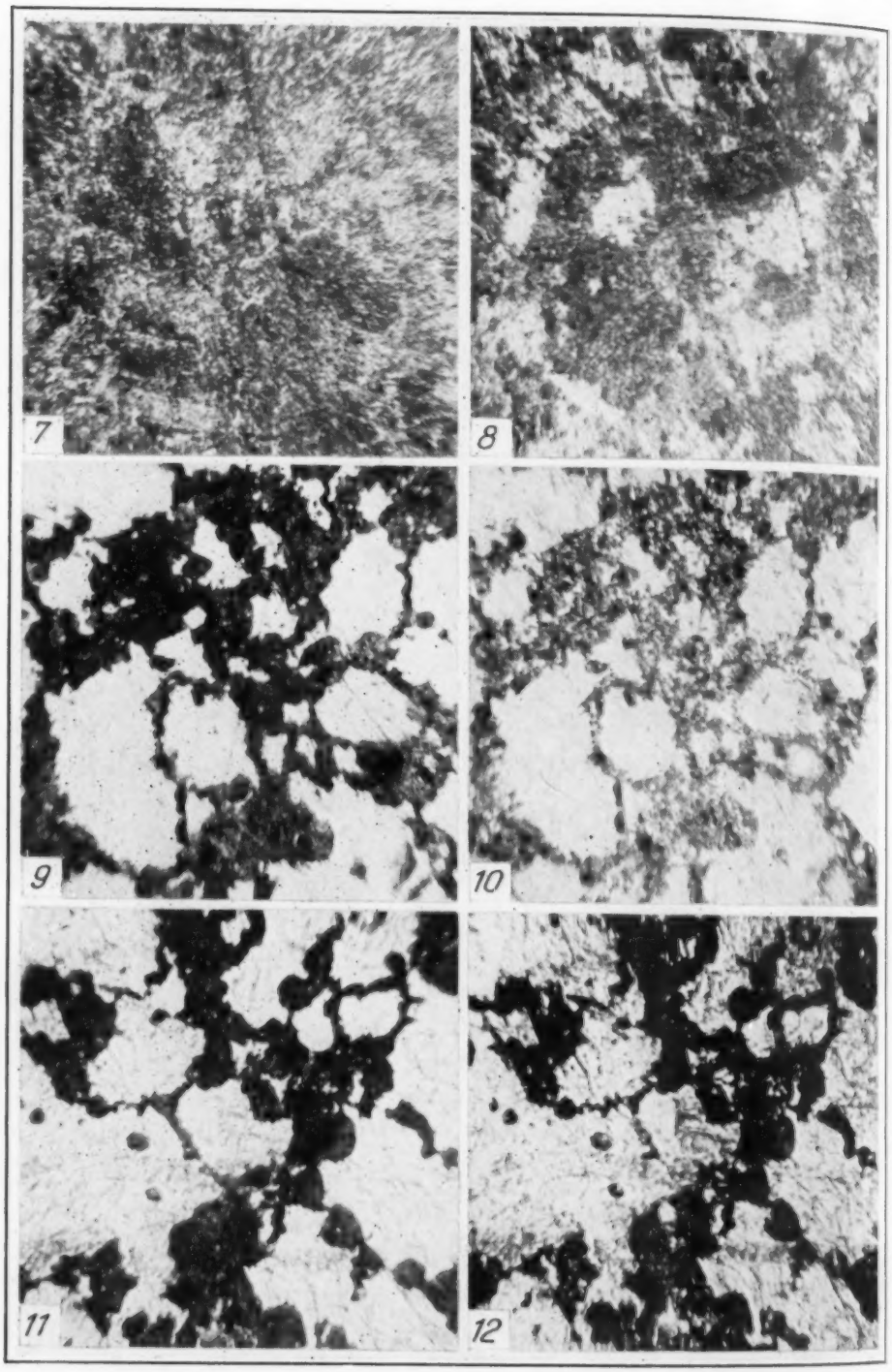
Figs. 5 and 6—Structure of α-Martensite in Parallel and in Polarized Light. All Photomicrographs × 190.

term "grain" is applicable in this instance, as the grain boundaries are not well defined. Often the dark areas in α–martensite become confluent with neighboring parts upon rotating the microscopic stage. The mechanism of transformation of austenite to α–martensite as proposed by Kurdjumow and Sach(12) should lead us to expect grain boundaries to be somewhat regular, but this was not the case. On the other hand, twins in α–martensite appeared frequently (Figs. 5, 6 and 15), although most of them were either badly deformed or incompleted. It should be mentioned here that in order to avoid unnecessary duplication of photomicrographs, it is understood that the nature of the twins and of anistropism is to be judged only from an actual study of the sample under polarized light upon rotating the stage. For example, in Fig. 15 upon rotation, the light and dark portions are reversed.

An attempt to ascertain if α–martensite is formed from austenite by a mechanism analogous to the Widmanstatten structure proved fruitless. It was observed, however, that the extinction angles of α–martensite were never sharp, that they were undulating. For this reason alone, it is doubtful if the value of c/a can ever be correlated with the maximum angle of extinction. The undulating nature of the extinction implies some kind of nonhomogeneity in α–martensite with respect to the concentration of Fe_3C dissolved (such as the case of zonal growth in quartz and other minerals).

II. *β–Martensite*—The samples in the α–martensite condition were annealed at 120 degrees Cent. (250 degrees Fahr.) for two days and the resulting structure is shown in Figs. 7 and 8. Anisotropism is very much more pronounced, evidently indicating the precipitation of an anisotropic substance from solid solution. Acccording to Honda and his associates(13) β–martensite is another solid solution of carbon in α–iron. If this were the case, the anisotropism observed in α–martensite should disappear when the sample is heat treated at 120 degrees Cent. (250 degrees Fahr.) as β–martensite is formed. When the samples were heat treated at about 300 degrees Cent. (570 degrees Fahr.) in order to decompose austenite, anisotropism became even more pronounced.

The question then arises as to how to differentiate between anisotropism due to α–martensite and that due to the presence of an orthorhombic Fe_3C colloidally dispersed in α–iron. The first differentiation is the undulating character of extinction in the former,



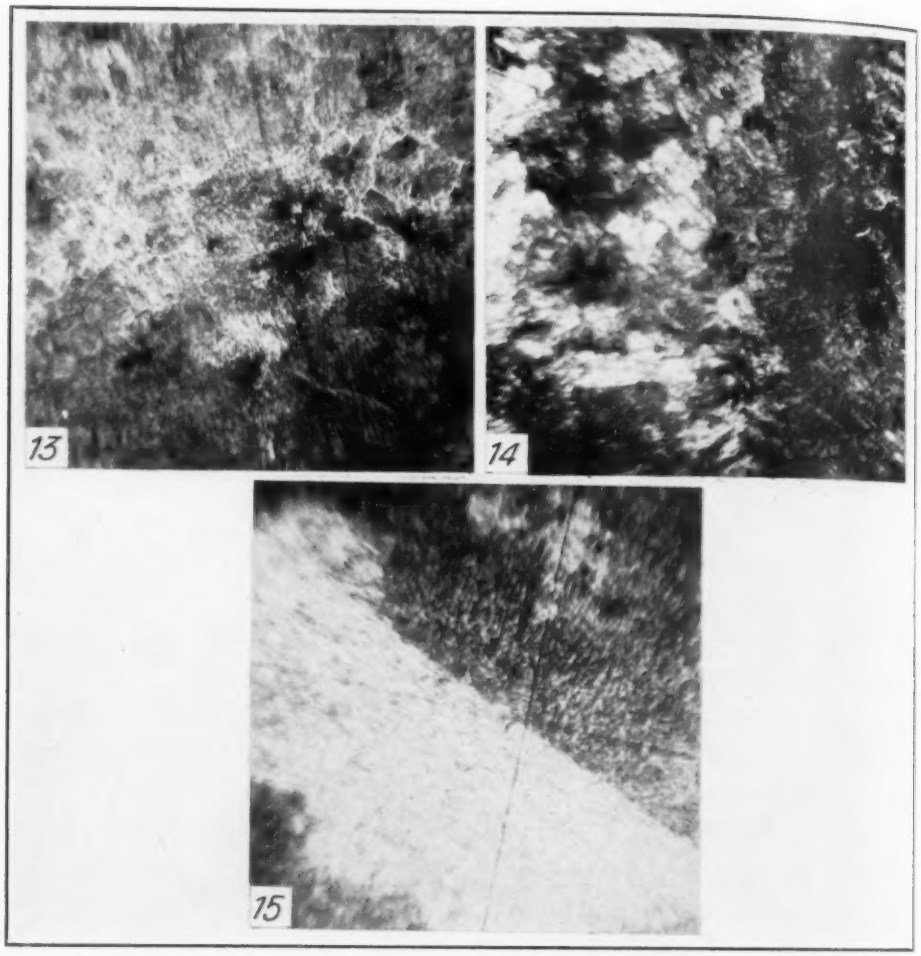
Figs. 7 and 8—Structure of β-Martensite in Parallel and in Polarized Light.
Figs. 9 and 10—Structure of Troostite in Parallel and in Polarized Light. The Sample was Etched Very Lightly in Order to Leave the Colloidal Fe_3C Undisturbed in the Structure.
Figs. 11 and 12—Same as in Figs. 9 and 10, but More Deeply Etched. Note the Similarity, Indicating Relative Absence of Anisotropism. Photomicrographs × 190.

which is not observed in the latter. The more important distinction is, however, that while the α–martensite has only two extinctions β–martensite has four, two strong ones and two weak ones. Taking into account the fact that the Fe_3C is colloidally dispersed in ferrite, one should not be surprised to note its behavior as a transparent substance. The presence of highly dispersed Fe_3C in quenched steel has been amply demonstrated by Lucas(14).

III. *Troostite*—Under ordinary parallel light, troostite apppears homogeneous at low magnifications, although Lucas(14) has shown it to be a heterogeneous mixture of ferrite and unresolved Fe_3C. In polarized light, the presence of an anisotropic substance in troostite is quite obvious, although it is quite difficult to show this condition satisfactorily in the photomicrographs (Figs. 9 and 10). When the steel sample is etched more deeply in order to remove the colloidal Fe_3C the anisotropic character of troostite becomes less evident (Figs. 11 and 12). Hence it appears reasonable to conclude that it is the presence of Fe_3C which gives rise to anisotropism in troostite. Radiating laminations of what appeared to be Fe_3C were sometimes observed at a magnification as low as 400, in polarized light. The structure shows some differential light absorption and four extinctions.

IV. *Pearlite* — The structure appears highly colored under polarized light, although extreme care was observed to prevent any tarnishing of the polished surface. The structure is highly anisotropic (Figs. 13 and 14) and has four extinctions accompanied by changes in color, thus weak extinction, blue, strong extinction, red, weak extinction, blue, strong extinction, red and then back to the weak extinction. The term "pearlite grain" is really, in the light of the writer's observations, somewhat of a misnomer and should be replaced by the term "pearlite segregate," as the segregates may be composed of several units of definite though gradual change in orientation. The latter form gives rise to marked undulating changes in the color and intensity of the light in crossed nicols. Likewise, we should be more consistent if we apply the term segregate to α–martensite.

V. *Spheroidized Cementite*—The spheroidized cementite appears to be isotropic in polarized light, although we know from X-ray crystal analysis that it crystallizes in the orthorhombic system. It was discovered, however, that when the sample was etchd more deeply



Figs. 13 and 14—Structure of Pearlite in Parallel and Polarized Light. Difficult to Photograph in Polarized Light on Account of Light Absorption. All Photomicrographs × 190.
Fig. 15—Evidence of Twinning in α–Martensite. × 400.

with a 5 per cent nital solution, the cementite particles showed anisotropism at higher magnifications (e.g., × 400).

It will be evident from an examination of the photomicrographs included in this paper that the microscopic examination of alloy structures should in the future include some study in polarized light. Thus, it has been shown that while α–martensite is an anisotropic solid solution, β–martensite is not a solid solution, as claimed by Honda. In β–martensite the Fe_3C in solid solution in α–martensite is precipitated, as was found by Lucas (microscopic evidence) and Öhman(15) (X-ray analysis).

One of the most interesting problems in physical metallurgy

is the cause of hardness, particularly of quenched steels. In a symposium conducted by Sauveur(16) the hardness of martensite is attributed to, first, solid solution of carbon or carbide in α–iron in a supersaturated state, resulting therefore in profound lattice distortion and internal strains; second, fineness of martensite grains; and third, presence of colloidal Fe_3C, thus offering tremendous slip obstruction. Let us now examine these different theories in the light of our information from the present study. Although α–martensite is undoubtedly a solid solution, no direct evidence has ever been produced to show that it is extremely hard. All methods of testing the hardness of metals involve deformation which would cause the decomposition of α–martensite to β–martensite. As Lucas first observed, incautious polishing is enough to cause such a decomposition as shown by his photomicrographs. On the other hand, we know that the decomposition of α–martensite takes place at as low as 100 degrees C., yet the hardness often increases slightly, while we should actually expect a large decrease in hardness. What apparently has been entirely overlooked is the fact that the presence of an extremely unstable transition phase (i.e., α–martensite) is itself sufficient evidence that the internal strains due to quenching have thereby been relieved.

We must, therefore, look for the hardness of quenched steel in some unusual condition of the α–iron and the iron carbide, inasmuch as β–martensite is not a solid solution. The broadening of the X-ray spectral lines of martensite has been generally attributed (e.g., Westgren(17)) to the fineness of the ferrite, on the assumption that the visible crystals of martensite are further composed of a large number of small elementary crystals. According to Honda and his associates(18) the diffuseness of the spectral lines is due to tremendous internal strains, while Heindlhofer and Bain(9) also came to practically the same conclusion. In the light of the evidence obtained in the present study, martensite is not fine-grained, so that the lattice strain theory appears the more probable at first sight. However, as we know that the recrystallization of highly strained metals takes place over some very small range of temperature and as the recrystallization temperature of the ferrite in quenched steels is in the neighborhood of 500 degrees Cent. (930 degrees Fahr.) according to Sato we should, therefore, expect a large drop in the hardness when the steel sample has been tem-

pered at that temperature. Yet the decrease in hardness is quite regular. Moreover, the diffuseness of the spectral lines practically disappear in samples tempered at 300 degrees Cent. (570 degrees Fahr.), well below the recrystallization temperature. It might be in order to give an alternative explanation of the diffuseness of the spectral lines. The normal solubility of Fe_3C in α–iron is about 0.04 per cent carbon, but on account of the surface energy of the highly dispersed Fe_3C, the solubility may be increased considerably. Lastly, since the particle size may not be constant the supersolubility will vary within the sample. The writer has shown(19) that the hardness of quenched steel is probably due to the surface energy of the highly dispersed Fe_3C, and that all precipitation hardening can be accounted for on that assumption.

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FURTHER EXPERIMENTS ON THE FORGEABILITY OF STEEL

By O. W. Ellis

Abstract

Earlier work on the forgeability of steel is reviewed, and the objects of the present investigation are discussed.

These objects were: (1) a detailed study of the influence of carbon on the forgeability of steel, using larger samples than have hitherto been employed; (2) a study of the effects of nickel, chromium, etc. on the forgeability of steel, using steels of various S.A.E. specifications; and (3) a study of the effects of melting practice on the forgeability of eutectoid steel.

The methods of test are described in detail, and forgeability-temperature curves are given for a number of steels.

Carbon is shown to have more profound effect on forgeability than nickel, chromium, etc. Nickel, chromium, and nickel plus chromium appear to have a greater effect on the forgeability of medium carbon steels than of low carbon steels. Variations in melting practice do not appear to affect the forgeability of steel as determined by the drop test. The method for determining the energy required to produce a definite deformation in a normal sample of steel, given the results of one drop test, is described in detail.

Introduction

IT IS now twenty-two years since Robin[1] offered the results of a considerable investigation on the resistance of steels to crushing as a *Carnegie Scholarship Memoir* to the British Iron and Steel Institute. The author feels that this classical work has never received the attention which it undoubtedly merits. While it is true that the manner in which Robin obtained and presented his results is open to criticism, certain of his observations, had they been ap-

[1]Robin, "The Resistance of Steels to Crushing," Iron and Steel Institute, *Carnegie Scholarship Memoirs*, Vol. II, 1910, p. 70.

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plied to practice, would unquestionably have eliminated the useless expenditure of a large amount of energy in both smithy and forge shop during the past quarter century.

Robin's experiments were conducted on a number of alloys, some ferrous and some nonferrous, at temperatures which ranged

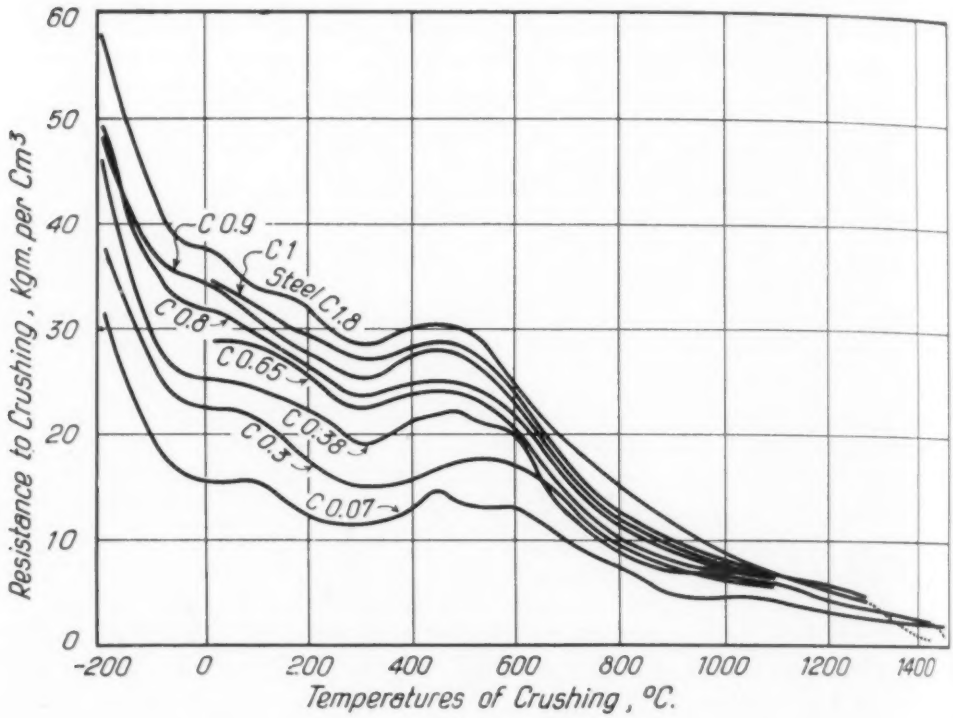


Fig. 1—Resistance of Carbon Steels to Crushing (Robin).

from —185 to +1100 degrees Cent. (—300 to 2010 degrees Fahr.). From the results of these experiments he estimated the amount of energy required to reduce normal cylinders (cylinders whose heights and diameters are equal) of these materials by 20 per cent of their original height. In this connection the results of Robin's work on the resistance to crushing of a number of straight carbon steels may be of interest. Hence Fig. 1, which indicates the importance of carbon in this connection, has been reproduced from page 144 of Vol. II of the *Carnegie Scholarship Memoirs*. From this it will be seen that all that can be directly arrived at from Robin's tables and curves is information regarding the amount of energy required to produce a certain definite alteration in the form of a cylinder of metal or alloy of a certain definite shape and size.

Effects of Critical Ranges of Steels Upon Forgeability

The possible effects of the critical ranges of steels upon their resistance to crushing were not considered by Robin, but in 1924 and 1926 Ellis[2] published the results of investigations into the effects of

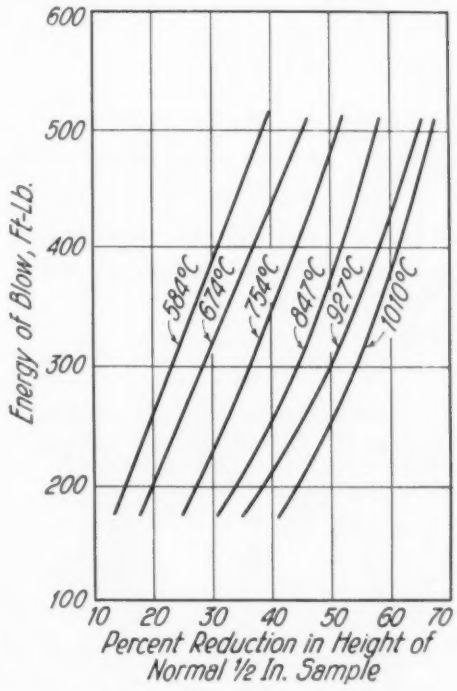


Fig. 2—Relationship between Energy of Blow Applied to and Percentage Deformation of Normal Samples of a 0.40 Per Cent Carbon Steel.

constitution on the forgeability of steel at high temperatures and showed clearly that the critical ranges had a very important influence in this connection.

At the same time Ellis determined the relationship between the energies of the blows applied to normal samples of a series of straight carbon steels and the amounts by which they were deformed. For each of the steels he examined he obtained families of curves, such as are shown in Fig. 2, which presents in graphical form the results of a number of tests on a steel containing 0.40 per cent carbon. He confirmed Robin's general observations in regard to the

[2]O. W. Ellis, "An Investigation into the Effect of Constitution on the Malleability of Steel at High Temperatures," Part I, Iron and Steel Institute, *Carnegie Scholarship Memoirs*, Vol. 13, 1924, p. 47; Part II, Iron and Steel Institute, *Carnegie Scholarship Memoirs*, Vol. 15, 1926, p. 195.

effect of carbon on the forgeability of steel at temperatures between 550 and 1000 degrees Cent. (1020 and 1830 degrees Fahr.), finding that carbon tended to increase the resistance of steel to plastic deformation at any given temperature.

Effect of Elements Other Than Carbon on the Forgeability of Steel

Robin found that phosphorus had a marked effect on the resistance of steel to plastic deformation, the forgeability of a steel containing 0.06 per cent carbon and 1.0 per cent phosphorus being of the same order as that of a 0.40 per cent carbon steel containing the more usual proportions of the nonmetal. He also investigated

Table I

Energy (ft. lb.) Required to Reduce Normal Cylinders (15 mm. x 15 mm.) of Steels of Various Types to 80 Per Cent of Their Original Height

Temperature Degrees Cent.	1.0% C Steel	1.0% C, 2.0% Cr Steel	0.3% C Steel	0.3% C, 2.5% Ni Steel	0.12% C Steel	0.1% C, 5.0% Ni Steel
500	513	522	313 ?	486	221	436
600	427	455	306 ?	432	207	360
700	...	337	230	243	180	...
800	229	295	170	163	127	154
900	184	216	133	.	94	...
1000	146	173	108	121	88	120
1100	115	153	91	121	83	...

(N.B.—Marks of interrogation in the fourth column are reproduced from Robin's original paper. Their significance is not known to the author.)

the effects of other elements on the forgeability of steel, but his presentation of the results of this part of his work is not altogether satisfying to one interested in the working of steel at temperatures above the critical range. Table I embodies the results of some of his tests on alloy steels, together with those of his tests on straight carbon steels of approximately the same carbon content.

The volume of the normal[3] samples tested by him was 0.162 cubic inch.

[3]A normal sample is one in the form of a cylinder whose height and diameter are equal.

Tresca's Theorem and Its Application in the Present Investigation

In Robin's paper he emphasized the value of Tresca's theorem in estimating the amount of energy required to produce analogous changes of shape in geometrically similar bodies. According to Tresca, this energy varies as the volumes or weights of the bodies concerned, provided, of course, that the bodies are similar in chemi-

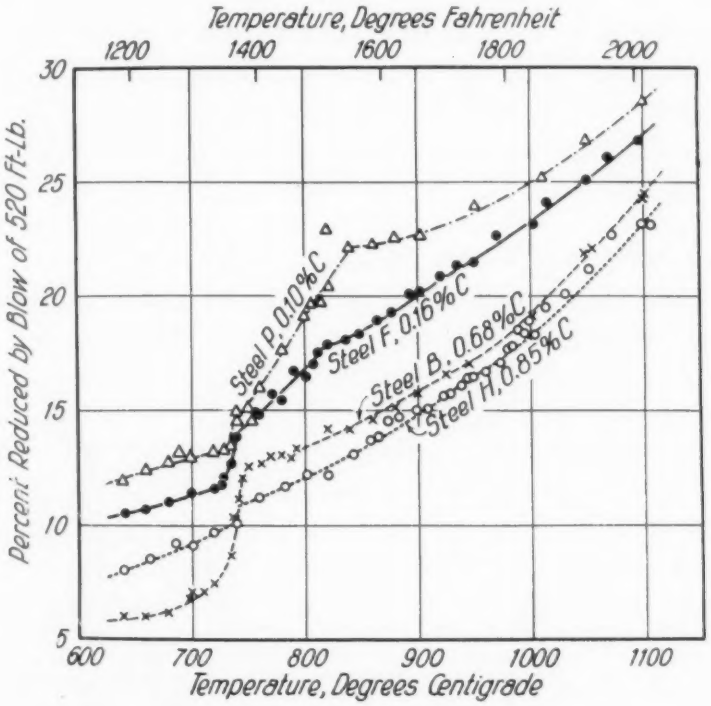


Fig. 3—Effect of Carbon on Forgeability of Carbon Steels.

cal and physical condition. Assuming Tresca's theorem to be true, one would expect that, other things being similar, the energy required to produce a given percentage reduction in the height of a normal sample, 1 inch in diameter, would be approximately 4.85 times that required to effect a similar reduction in a normal sample of the same metal, 15 millimeters in diameter, since the volume of the former sample is 4.85 times that of the latter.

In the first of the present author's papers referred to above he showed that Tresca's law was true insofar as the tests described therein were concerned. That Tresca's law is true for certain, if not all, of the results quoted in this paper may be shown by comparing, for

example, the energy required to reduce by 20 per cent in height the 15 millimeter normal sample of 1.0 per cent carbon steel referred to in Table I with that required to reduce the 1-inch normal sample of 0.85 per cent carbon steel, results of the tests on which are shown in Fig. 3. The latter was reduced by 20 per cent in height at a temperature of 1040 degrees Cent. (1905 degrees Fahr.), the energy of the blow being 520 foot-pounds. Tresca's law would lead to the view that a 15 millimeter normal sample of the same steel should require $520/4.85 = 107$ foot-pounds of energy to deform it by the same amount at the same temperature. Reference to Table I will show that approximately 134 foot-pounds were required to deform the 1 per cent carbon steel dealt with by Robin. The difference between the estimated 107 foot-pounds and the observed 134 foot-pounds can probably be accounted for by the higher carbon content of Robin's steel.

A further example may be cited. The 0.10 per cent carbon steel tested by the author (see Fig. 3) was reduced 20 per cent in height at a temperature of approximately 815 degrees Cent. (1500 degrees Fahr.) under a blow of 520 foot-pounds energy. Robin's 0.12 per cent carbon steel sample (Table I) should have required, roughly, 107 foot-pounds of energy to reduce it 20 per cent at the same temperature. Reference to Table I will show that the observed energy required to effect this deformation was approximately 122 foot-pounds. Here, again, the difference in carbon content probably accounts for the slight excess in energy over the estimated amount of 107 foot-pounds.

The fact that such close agreement exists between the results obtained by Robin and those obtained by the author, when considered in the light of Tresca's theorem, lends some support to the view that, at any rate, insofar as the straight carbon steels are concerned, the methods which have been used by Robin and the author in determining the forgeability of steels at various temperatures are generally satisfactory.

Objects of Present Investigation

(1) Most of the experiments carried out by the author in his previous investigations were made on ½-inch normal samples of steel. These samples being somewhat small, he wished to discover, if possible, whether the same general effects would be observed, were larger samples to be used. He had every reason to suppose that

such would be the case, in view of the closeness with which he had already checked the work of Robin on the 15-millimeter normal samples referred to. Nevertheless, he felt that further work on the straight carbon steels was in order. Hence a study was made of the forgeability-temperature relationships of four typical straight carbon steels (see Fig. 3), the size of normal sample being 1 inch and the energy of blow throughout the entire series of experiments being 520 foot-pounds.

(2) Apart from Robin, no one appears to have investigated the forgeability-temperature relationships of any of the alloy steels. In view of what has already been said in this connection, the author felt that an investigation of a few typical alloy steels would be well worth while. Tests, therefore, were made on normal 1-inch samples of seven alloy steels, the energy of blow throughout the entire series of tests being 520 foot-pounds as above.

(3) Evidence has been produced, which appears to indicate that the forgeability of steel of constant analysis is affected in a pronounced manner by variations in melting practice. Through the courtesy of Dr. H. B. Allen, chief metallurgist of Henry Disston and Sons, Inc., the author was enabled to determine how far such variations in forgeability as were produced by alterations in melting practice could be detected by means of the drop test.

Description of the Experiments

All the present experiments were conducted on test samples 1 inch high and 1 inch in diameter. The blows were applied to the samples by means of a hammer weighing 113 pounds. This hammer was allowed to fall from a height of 55½ inches to the top of the test sample. The energy of the blow applied to the samples was, therefore, 520 foot-pounds.

A picture of the apparatus used in these tests, showing its relationship to the furnace in which the samples were heated, is shown in Fig. 4.

The samples were heated to the forging temperatures in a Globar furnace, which could be controlled within relatively close limits by means of a Bristol pyrometer controller. This controller was set in such a way as to hold the furnace at constant temperature. When this constant temperature had been reached, 3 samples were placed within the furnace in close proximity to the hot junc-

tion of the controlling pyrometer. One of these samples had been drilled to a point a little over half way through. Into this hole the hot junction of another pyrometer was snugly fitted, so that the tem-

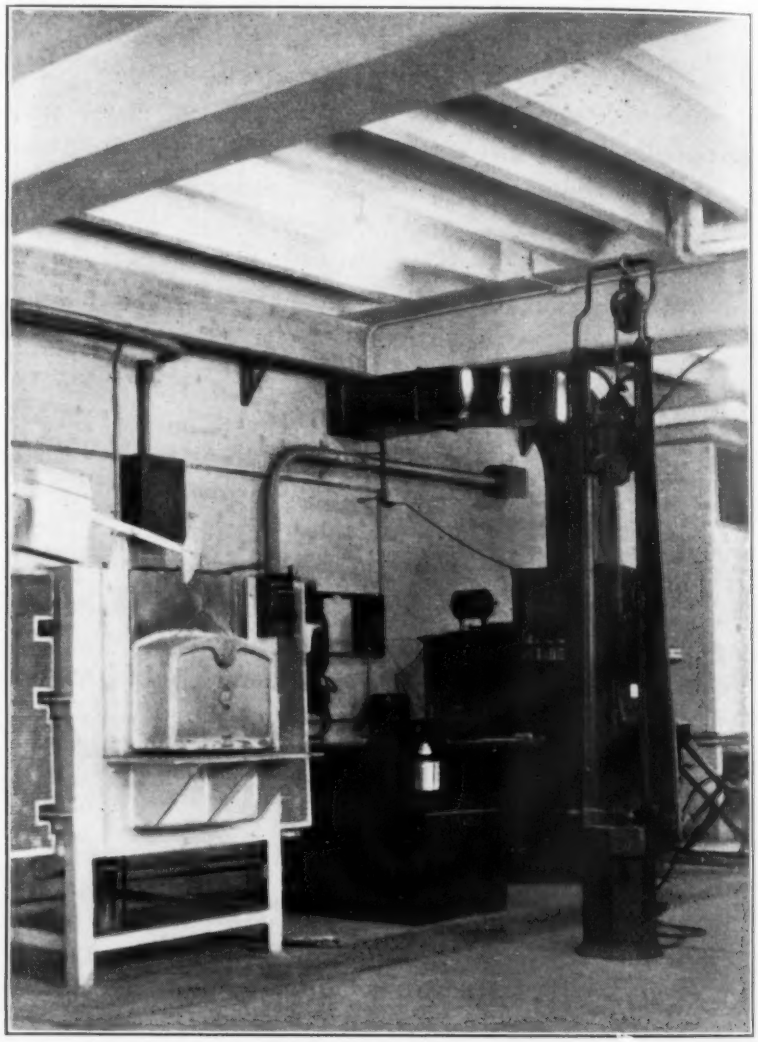


Fig. 4—Photograph of Apparatus Used in These Tests Showing Its Relationship to the Furnace in Which Samples Were Heated.

perature of this sample could be observed by suitable means outside the furnace. A Cambridge workshop potentiometer was used in this connection.

When the temperature of the sample into which the pyrometer was fitted had remained constant for a period of approximately five minutes, one of the other samples was immediately withdrawn from the furnace, placed on the anvil of the drop-hammer, and subjected

to a blow from the tup. The sample was allowed to remain under the tup until cool. The furnace door was closed immediately after the first undrilled sample was removed. When forging had been completed, the furnace door was raised and the other undrilled sample was taken from the furnace and quenched in water at 20 degrees Cent. (68 degrees Fahr.). At the same time the drilled sample, into which the hot junction of the recording thermocouple had been fitted, was removed from the furnace and allowed to cool in air.

The object of quenching one of the samples was to confirm the position of the critical range as determined by the forging experiments. It was assumed, and was found to be true, that a marked increase in hardness would coincide with the somewhat radical change in the forgeability-temperature relationship for the various steels being investigated.

It had been shown in our previous experiments that the transference of samples, even so small as half an inch in diameter, had little if any effect upon the temperature of the sample relative to that recorded within the furnace. In other words, the temperature of the samples in the present experiments did not change appreciably during their transference from the furnace to the anvil.

After the forged sample had cooled to room temperature, its height was measured. Its initial height being known, the height after forging was subtracted from the initial height and then divided by the initial height in order to obtain (by multiplying the above value by 100) the percentage reduction in height due to forging at the particular temperature at which the sample had been deformed.

Forgeability-Temperature Relationships for Straight Carbon Steels

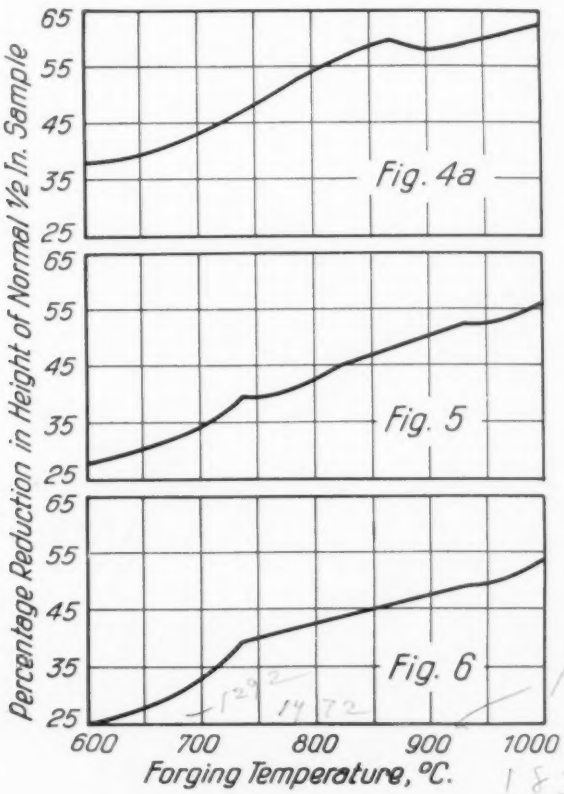
Using 1-inch normal samples, tests were conducted on a series of straight carbon steels of the following analyses.

Element	Steel P	Steel F	Steel B	Steel H
Carbon	0.10	0.16	0.68	0.85
Silicon	....	0.13	0.19	0.28
Manganese	0.44	0.54	0.57	0.29
Sulphur	0.037	0.028	0.022	0.011
Phosphorus	0.018	0.017	0.027	0.027

The results of these tests are shown in Fig. 3. A study of this diagram will indicate how clearly the positions of the critical points

of these four steels are brought out by such tests as have been described above.

These curves differ in some respects from those which were obtained by the author in 1924, using ½-inch normal samples. In 1924, tests on a steel containing 0.08 per cent carbon showed it to



Figs. 4a, 5, and 6—Effect of Carbon Content on the Forgeability of Three Different Steels. 4a—0.08 Per Cent Carbon, 5—0.40 Per Cent Carbon, 6—0.56 Per Cent Carbon.

decrease quite distinctly in malleability at temperatures just beyond the upper critical point, as is shown in Fig. 4a reproduced from the author's earlier paper.

The forgeability-temperature relationships for straight carbon steels, containing 0.40 and 0.56 per cent carbon, respectively, and tested in the form of ½-inch normal samples, are shown in Figs. 5 and 6, also reproduced from the author's 1924 Carnegie Scholarship memoir. Examination of these will show that a distinct inversion in the curves of these steels occurs at a temperature in the neighborhood of 930 degrees Cent. (1705 degrees Fahr.). No such inversion

can be detected in the curves for the straight carbon steels shown in Fig. 3.

It is not impossible that the larger samples (which were less deformed during test than the ½-inch normal samples used by the author in his previous experiments) are less satisfactory for the pur-

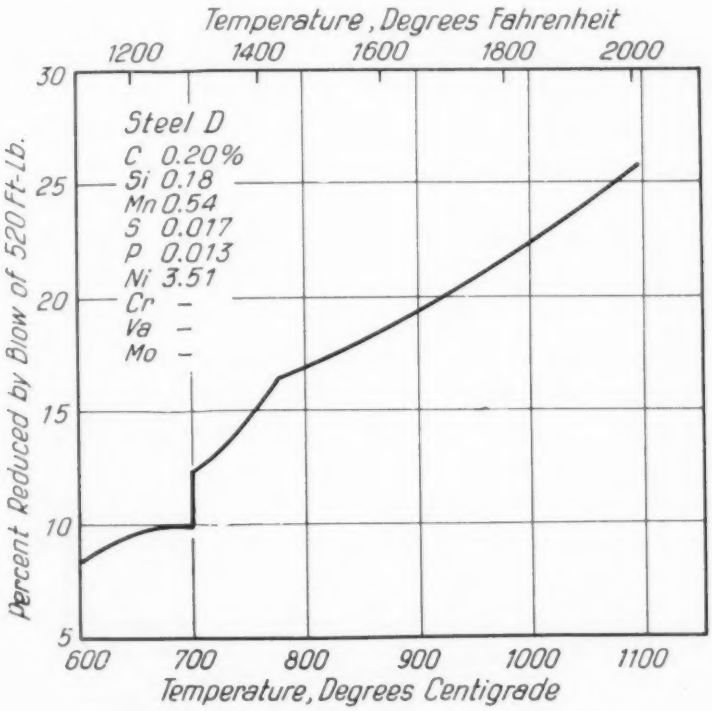


Fig. 7—Forgeability-Temperature Curve for Steel D.

pose of bringing out the finer details of the forgeability-temperature relationships for steels generally.

On the other hand, the present tests have brought out the position of the A_1 point in these steels far more clearly than the previous tests, in which the ½-inch normal samples were used.

It is scarcely necessary to discuss in detail the curves shown in Fig. 3. The fact that carbon has a profound effect upon the forgeability of steel is quite clearly indicated by the curves. One point of interest may be referred to—namely, that at temperatures below the critical range the 0.68 per cent is far less malleable than the 0.85 per cent carbon steel. The latter was doubtless annealed; the former was in the "as-rolled" condition when received and as tested. Hardness tests of these steels as received showed the former to have a Brinell number of 205, and the latter a Brinell number of 175. Had

the 0.68 per cent carbon steel been annealed prior to test, its curve at temperatures below the critical range would have fallen between the curves for steels F and H rather than below that for steel H, as shown in Fig. 3.

Effect of Special Elements on the Forgeability of Steel

As already stated, Robin investigated the effect of certain elements on the forgeability of steel. It was felt, however, that further work along this line would be worth while, largely on account of the difficulty of applying the results of Robin's work to every-day practice.

A series of steels, in the form of 1-inch diameter rods, was obtained for the purposes of this part of our investigation. These steels were purchased from stock and were tested as received. No attempt was made to anneal the steels before forging, so that the effects of the structure of the steels, as received, upon their forgeability at temperatures below the critical ranges must be accounted for in any consideration of these results. Normally, of course, forging of steels takes place at temperatures above the critical range, so that the behavior of steels below the critical range need scarcely be considered in this connection.

It may be well to deal with the elements, insofar as it is possible to do so, in order, as below.

A—Nickel—The nickel steel used for the purpose of determining the effect of this element upon the forgeability of steel having a relatively low carbon content, was an S.A.E. 2320 steel of the following analysis:

	Per Cent
Carbon	0.20
Silicon	0.18
Manganese	0.54
Sulphur	0.017
Phosphorus	0.013
Nickel	3.51

The steel contained neither chromium, vanadium, nor molybdenum.

The forgeability-temperature relationship for this steel is shown in Fig. 7. Two things will be noted in this curve: (1) the way in which the A_1 point stands out, and (2) the way in which the A_3 point is shown.

With the view of indicating the effect of nickel upon the forgeability of low carbon steel Fig. 8 has been prepared. This shows, in one and the same diagram, the forgeability-temperature relation-

ships for the straight carbon steel F containing 0.16 per cent carbon (Fig. 3) and the nickel steel D (Fig. 7) just discussed.

From what has already been shown in Fig. 3 it will be clear that such differences as exist in the forgeability of these steels at temperatures above 800 degrees Cent. (1470 degrees Fahr.) can be ac-

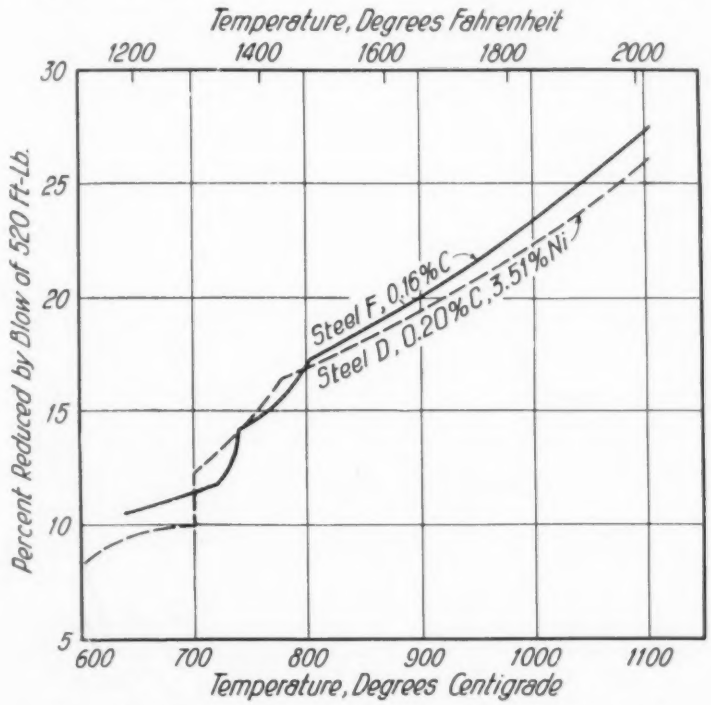


Fig. 8—Effect of Nickel on Forgeability of Low Carbon Steel.

counted for by the somewhat greater carbon content of steel D. To sum up, one may say with some confidence that the presence of 3.51 per cent of nickel has but little effect, if any at all, upon the forgeability of low carbon steel under the conditions of these experiments.

For the purpose of determining the effect of altering the carbon content of a nickel steel containing approximately 3.5 per cent of nickel, an examination was made of a steel to specification S.A.E. 2345. This steel (G) had the following analysis:

	Per Cent
Carbon	0.44
Silicon	0.22
Manganese	0.77
Sulphur	0.019
Phosphorus	0.015
Nickel	3.38

It contained neither chromium, vanadium, nor molybdenum.

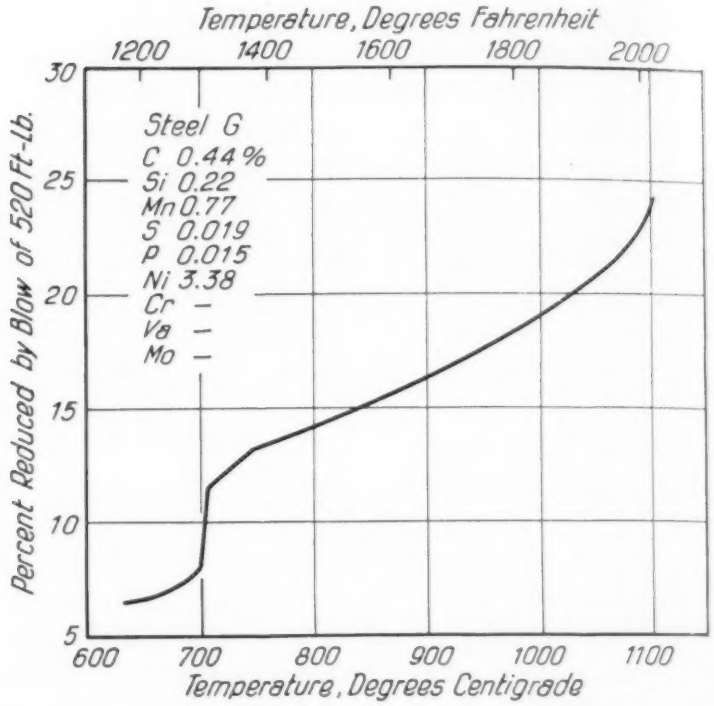


Fig. 9—Forgeability-Temperature Curve for Steel G.

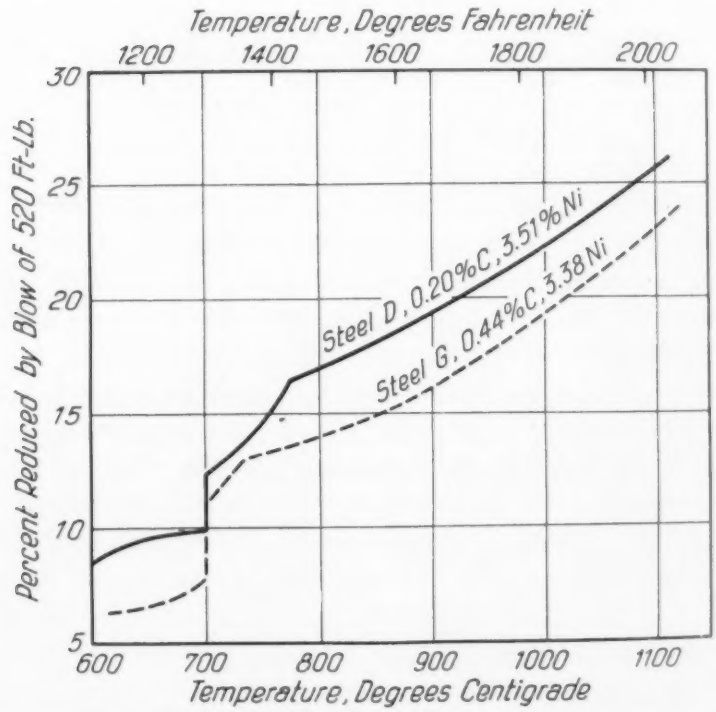


Fig. 10—Effect of Carbon Content on Forgeability of Similar Nickel Steels.

The forgeability-temperature relationship for this steel is shown in Fig. 9, and a comparison between the curves for steels D and G is shown in Fig. 10. The relative importance of carbon and of nickel in raising the resistance of steel to plastic deformation at temperatures above the critical temperature ranges can be readily judged from the latter.

A further diagram may be of interest in this connection. Fig. 11 shows the curves for steels B and G. The former is the 0.68 per

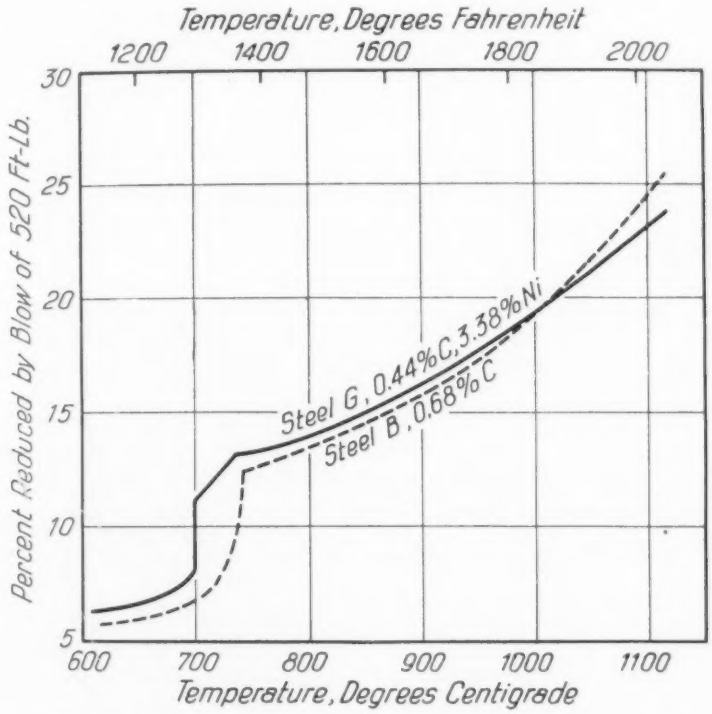


Fig. 11—Effect of Nickel on Forgeability of Medium Carbon Steel.

cent carbon steel of which the forgeability-temperature relationship was shown in Fig. 3, the latter the S.A.E. 2345 steel of which the forgeability-temperature relationship was shown in Fig. 9. These curves are reproduced for the purpose of indicating that a steel containing approximately 0.68 per cent carbon has a forgeability-temperature curve almost identical in general character with that of a steel containing 0.44 per cent carbon and 3.38 per cent nickel. From this it appears that the addition of nickel to medium carbon steel has the effect of increasing its resistance to forging, particularly at temperatures above 1000 degrees Cent. (1830 degrees Fahr.) or in that general range.

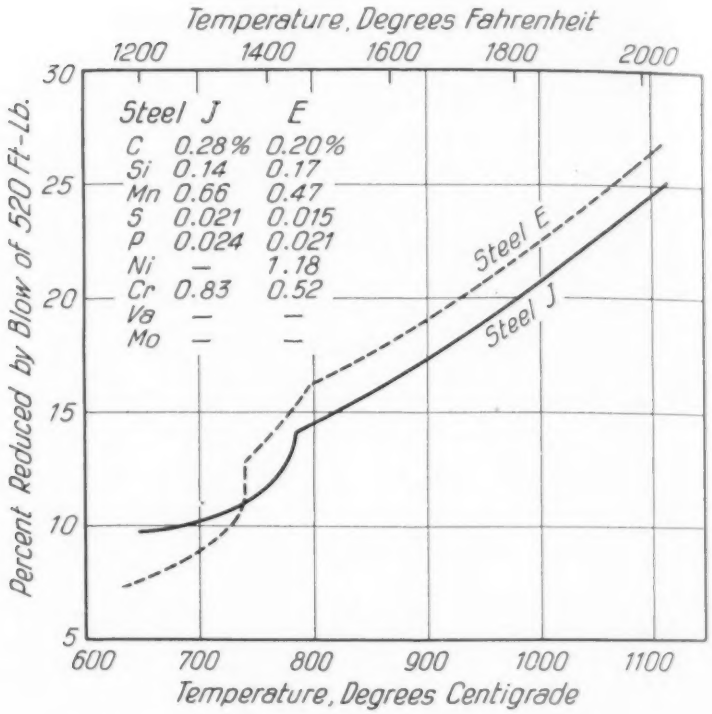


Fig. 12—Forgeability-Temperature Curves for Steels J and E.

B—Chromium—For the purpose of investigating the effect of chromium upon the forgeability of steel, material approximating steel S.A.E. 5130 was employed. It had the following analysis:

	Per Cent
Carbon	0.28
Silicon	0.14
Manganese	0.66
Sulphur	0.021
Phosphorus	0.024
Chromium	0.83

and contained neither nickel, vanadium, nor molybdenum. The forgeability-temperature relationship of this steel (J) is shown in Fig. 12. A comparison of this curve with those in Fig. 3 has shown it to lie between the curves for steels F and B and actually to intersect the curve for steel B at a temperature of about 1100 degrees Cent. (2010 degrees Fahr.). In view of this fact one is led to believe that chromium must have a relatively profound effect upon the forgeability of steel. One cannot speak with authority, however, since no direct comparison was made between steels having approximately the same carbon content, the one with, and the other without, chro-

mium. Further, since the forgeability of steels containing relatively low amounts of carbon appears to be reduced by carbon far more rapidly than that of high carbon steels, the low forgeability of this chromium steel relative to the 0.16 per cent straight carbon steel (Fig. 3) may be due to the difference in carbon content rather than to the chromium content of the former.

C—Nickel plus Chromium—A series of steels containing nickel and chromium was investigated. These were of the following analyses:

Elements	Steel E Per Cent	Steel A Per Cent	Steel C Per Cent	Steel K Per Cent
Carbon	0.20	0.33	0.44	0.45
Silicon	0.17	0.23	0.19	0.22
Manganese	0.47	0.54	0.52	0.40
Sulphur	0.015	0.018	0.018	0.011
Phosphorus	0.021	0.013	0.022	0.027
Nickel	1.18	1.27	1.63	1.60
Chromium	0.52	0.70	0.99	1.03

They contained neither vanadium nor molybdenum.

Steel E falls in line with the specification for S.A.E. steel 3120, steel A with the specification for S.A.E. steel 3135, steels C and K with the specification for S.A.E. steel 3245. It will be noted that steels C and K were practically identical in composition. They were supplied as different in analysis, but, though found to be so similar, were tested completely with the view of determining to what extent results might be reproduced on different steels made of the same specification. Figs. 12 to 14, inclusive, show the forgeability-temperature relationships for these four steels.

Fig. 15 has been prepared with the view of comparing the effects of nickel and of nickel plus chromium upon the forgeability of steels of approximately the same carbon content. It will be noted that the curves for steels E and D, which have the same carbon content, but which differ quite appreciably in their nickel and nickel plus chromium contents, lie very close to one another throughout the entire range of temperatures above the A_3 points for these steels.

On the other hand, steel A, which contains 0.13 per cent more carbon than either of steels E or D, is distinctly more resistant to deformation above the A_3 point throughout the entire range covered by these experiments. One is led again to the view that carbon is far more potent in its effect upon the forgeability of low carbon steel than are either nickel or chromium, or these two elements combined.

It may be of interest to observe here that the curve for steel J, which contained 0.28 per cent carbon and 0.83 per cent chromium (see Fig. 12), lies very close to, though slightly below, the curve for steel A.

For the purpose of comparing steels C and K, Fig. 16 has been prepared, in which the forgeability-temperature relationships for

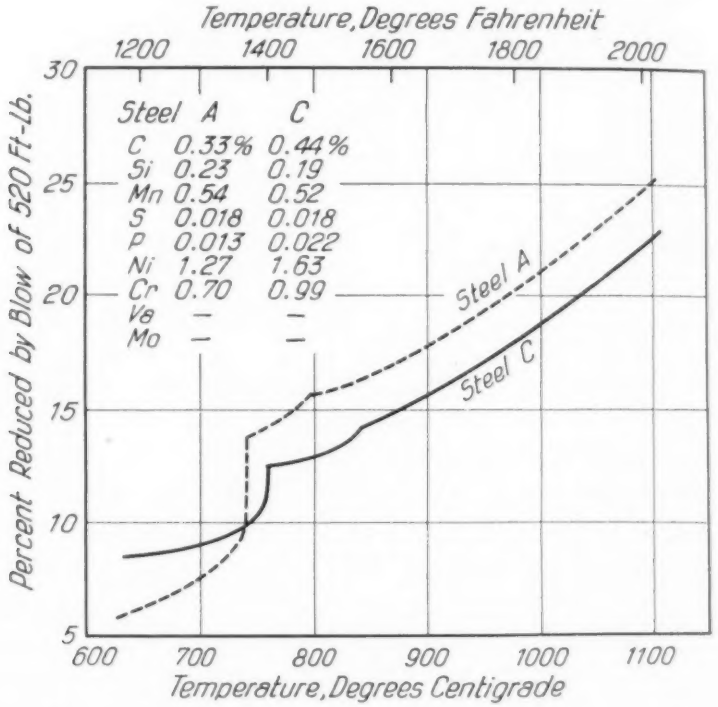


Fig. 13—Forgeability-Temperature Curves for Steels A and C.

these two steels have been plotted, so as to indicate clearly the differences between the results obtained on the two steels which, as already indicated, were of practically identical composition.

In this same diagram the curve for steel G, which contained 0.44 per cent carbon and 3.38 per cent nickel, has been reproduced. It will be seen from this that at temperatures above 850 degrees Cent. (1560 degrees Fahr.) the forgeability-temperature relationships for these three steels are nearly the same. The differences observed at temperatures below 850 degrees Cent. are due, in all probability, solely to the difference in the positions of the upper critical temperature points.

A comparison of the curves for the two nickel-chromium steels shown in Fig. 16 with those for the straight carbon steels shown in

Fig. 3 indicates that the forgeability of the former over the range of temperatures 800-1000 degrees Cent. (1470-1830 degrees Fahr.) approximates closely to that of the 0.68 and 0.85 per cent carbon steels. At 850 degrees Cent., the curves for steels C and K lie almost on the curve for the straight carbon steel B containing 0.68 per cent carbon; at 1100 degrees Cent. (2010 degrees Fahr.) the curves

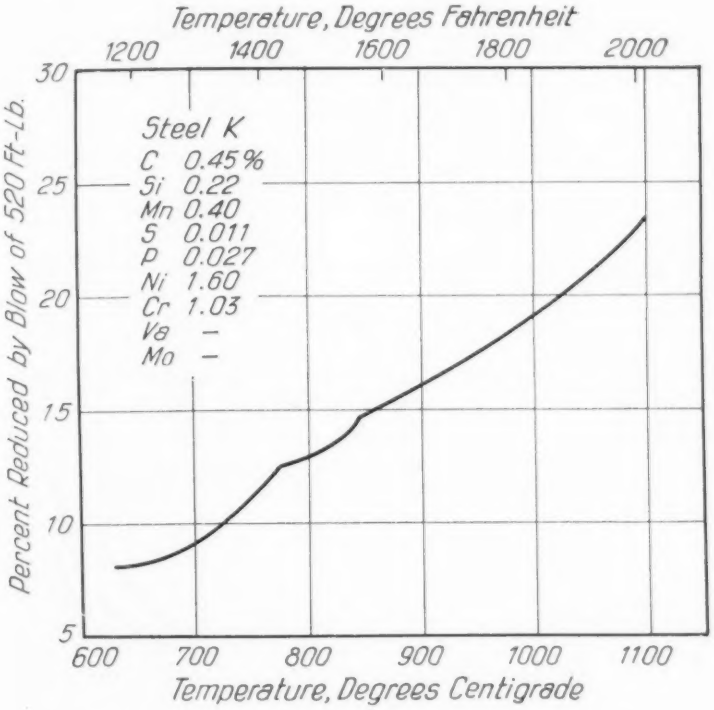


Fig. 14—Forgeability-Temperature Curve for Steel K.

for steels K and C lie almost exactly upon the curve for the straight carbon steel H containing 0.95 per cent carbon. One would judge from this comparison that the addition of 1.6± per cent nickel and 1± per cent chromium to a 0.45± per cent carbon steel has the effect of decreasing its malleability, this decrease being slightly greater at high temperatures than at low. The assumption is here made, of course, that the forgeability-temperature curve for a 0.45 per cent straight carbon steel would lie above the curve for steel B (0.68 per cent carbon) shown in Fig. 3.

D—Chromium plus Vanadium—For the purpose of determining what effect, if any, vanadium had upon the forgeability of an S.A.E. 5130 steel, tests were conducted on materials of the following analyses:

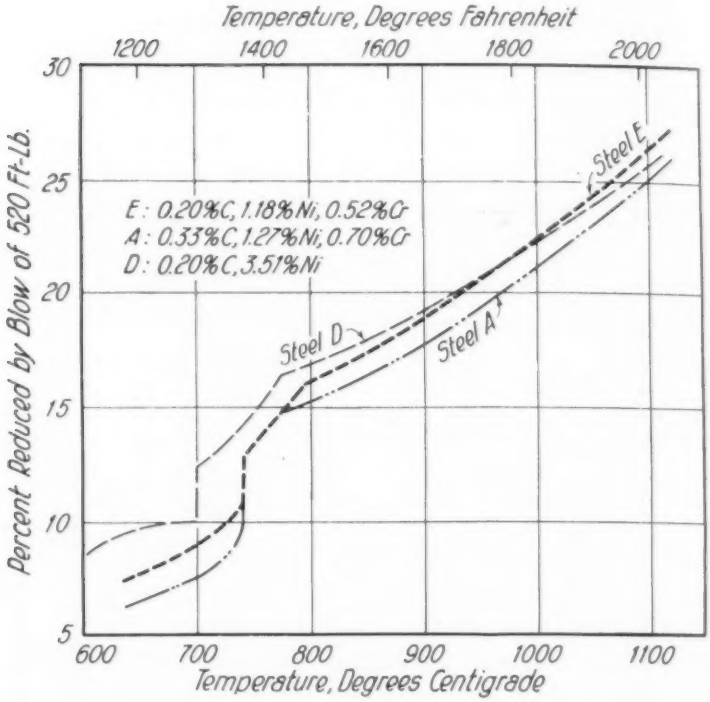


Fig. 15—Relative Effects of Carbon, Nickel and of Chromium plus Nickel on Forgeability of Steel.

Elements	Steel I Per Cent	Steel J Per Cent
Carbon	0.20	0.28
Silicon	0.20	0.14
Manganese	0.67	0.66
Sulphur	0.020	0.021
Phosphorus	0.022	0.024
Nickel	0.17	Nil
Chromium	0.90	0.83
Vanadium	0.142	Nil

Examination of the curve shown in Fig. 17 will demonstrate the similarity in the forgeability of these steels over the entire range of temperature above the critical range. One might be tempted to suggest that vanadium alters the rate of change of forgeability with temperature in view of the difference in slope of the two curves, but from what we have seen of the variations in results that can be obtained from two steels of practically the same analysis (see Fig. 16), one feels that it would not be altogether fair to put this forward as an explanation for the relative positions of the two curves in Fig. 17. The marked difference in malleability between the two steels at temperatures below the critical range can unquestionably be con-

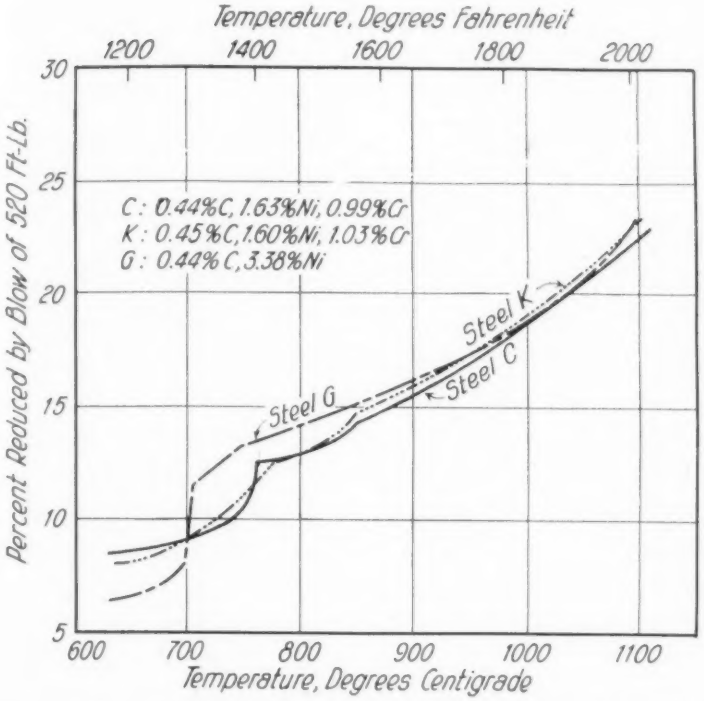


Fig. 16—Reproducibility of Test Results Using Different Steels and the Relative Effects of Nickel and Chromium.

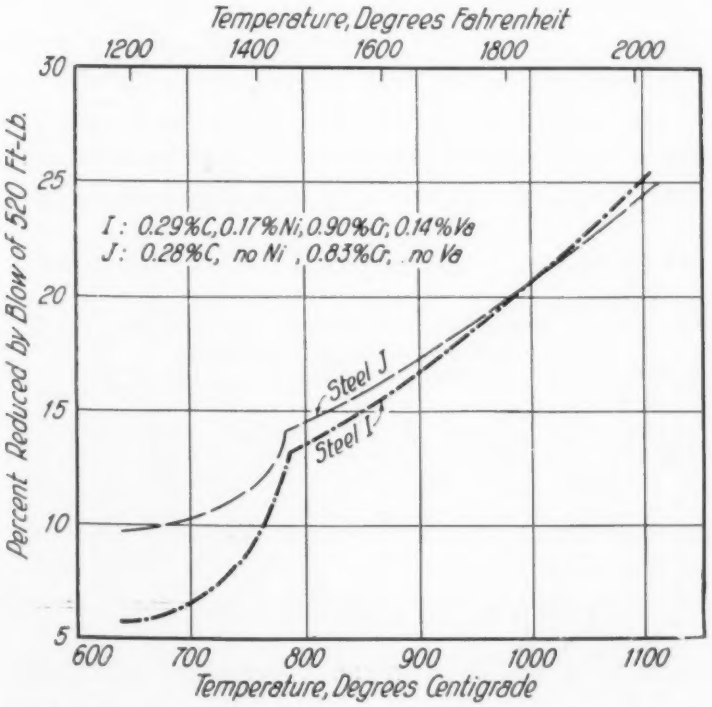


Fig. 17—Effect of Vanadium on the Forgeability of Chromium Steels.

sidered as due to the presence of vanadium in steel I. Hardness tests made on these steels in the "as-received" condition showed steel I to have a Brinell number of approximately 260, while that of steel J was approximately 140. Normalizing of these steels at a series of temperatures varying from 800 to 1090 degrees Cent. (1470 to 1995 degrees Fahr.) resulted in steel I invariably being harder than steel J.

E—Summary of Foregoing Results—It appears from the foregoing results that the addition of nickel, of chromium, or of nickel plus chromium to low carbon steel has but little effect upon its forgeability, whereas the addition of these elements to medium carbon steel has the effect of reducing their forgeability, possibly of reducing it more noticeably at high than at low temperatures. Tests on a greater number of steels would be required before any definite conclusions could be arrived at in this connection. The author has unfortunately been unable as yet to obtain a wider range of medium carbon steels for his experiments.

The Influence of Melting Practice, Etc., on the Forgeability of Steel

For the purpose of investigating the effect of variations in melting practice, etc., on the forgeability of steel of approximately constant analysis, the author used a series of steels, the compositions of which are quoted in Table II. These were supplied to him through the courtesy of Dr. H. B. Allen, chief metallurgist of Henry Disston and Sons, Inc., in the form of 1-inch round bars.

Table II

Analysis of Steels Examined for the Purpose of Determining the Effects of Melting Practice on Forgeability

Steel	C	Si	Mn	S	P	Ni	Cr	Mo	Manufactured in
M S H	0.88	0.26	0.32	0.016	0.022	0.08	0.07	....	Electric furnace
M S L	0.87	0.22	0.41	0.022	0.022	0.67	0.04	0.16	Open-hearth
M S M	0.90	0.20	0.33	0.022	0.012	0.07	0.07	....	Open-hearth
M S N	0.85	0.22	0.25	0.012	0.020	0.70	0.09	0.11	Electric furnace; charge contained 40 per cent sponge iron
M S O	0.88	0.24	0.29	0.013	0.022	0.65	0.12	0.14	Electric furnace; charge contained 13 per cent sponge iron

The results of the tests on these five steels are typified in Fig. 18. Examination of the results of these tests showed that steels H

and M, which were to all intents and purposes straight carbon steels, were practically identical in their forgeability at all temperatures above the critical range. Even below the critical range the similarity in malleability persisted. This only shows, however, that the steels had been brought to practically the same structural condition, e. g., by annealing, prior to the forging test. Steel L was practically

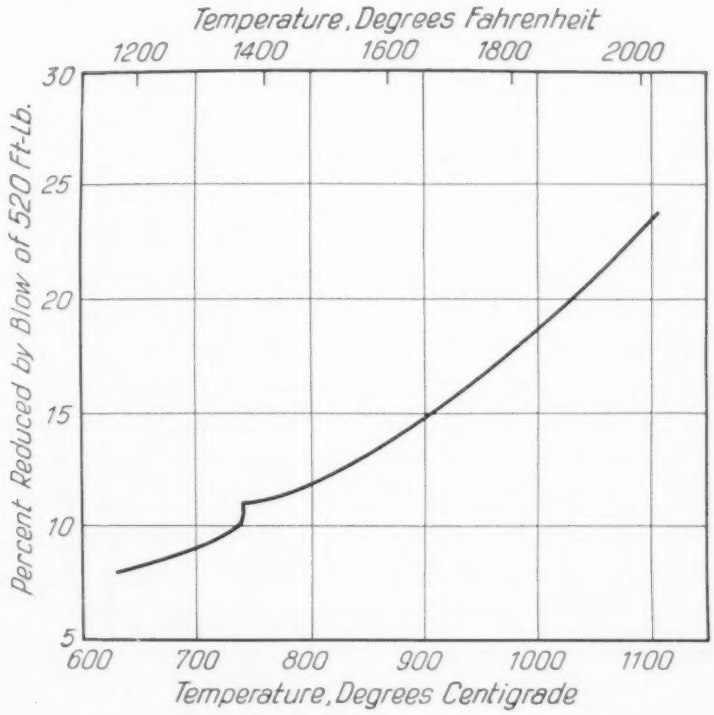


Fig. 18—Forgeability-Temperature Curve for Steel H.

identical with steels H and M at temperatures above the critical range, showing that the 0.67 per cent nickel and 0.16 per cent molybdenum present in this steel had little, if any, effect upon its forgeability. Below the critical range steel L was slightly harder than steels H and M.

Steel N was found to be only slightly harder than steels H and M, both above and below the A_1 point. The slight difference in hardness might best be neglected. It can scarcely be assumed that either the method of manufacture or the presence of sponge iron in the charge was effective in producing this difference.

Steel O was found to be slightly harder than steel N. In this case, again, neither the method of manufacture nor the presence of sponge iron in the charge can be considered to have influenced the

forgeability of the steel. In short, the forgeability-temperature relationships for steels H, L, M, N, and O are practically identical. This means either that the forgeability of steel of constant analysis is unaffected by such variations in melting practice as have been described in Table II, or that the drop test (using a weight of 113 pounds and a fall of 55½ inches to the top of the sample) is unable to distinguish such variations in the forgeability of 1-inch normal samples as are due to these causes.

Method for Determining the Energy Required to Effect a Definite Deformation in a Normal Sample of Steel

As may be judged from the above, the author has been interested in determining the energy required to produce certain definite alterations in shape of normal samples of various steels. Reference has been made to the work which he published in 1924, and Fig. 2 of the present paper has shown a family of curves representing the relationship between energy and percentage deformation at various temperatures for a series of steels containing 0.40 per cent carbon.

What the author feels to be one of the most important developments of his work has been the determination of a simple equation covering families of such curves. If E be the energy in foot-pounds required to produce a certain definite percentage reduction in height D of a normal sample, then E and D are related by the following equation:

$$E = bD^{(1.56-0.47 \log b)} \qquad (I)$$

b is a parameter which can be found by making one drop test.[4]

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[4]Much better results are obtained when the values for E and D are plotted on logarithmic paper, a linear relationship existing between log E and log D. In most cases the observed values for E and D lie close to the straight line drawn through an entire set of observations. In some cases, however, individual points lie away from the chosen line. An attempt has been made to determine the extent to which calculations of the value of E, based on such an individual point, would be in error. It was found in what was one of the worst cases that the value of E_c, i.e., E as determined from the straight line representing a series of observations, was related to the value E_o, i.e., E based on an individual erroneous point and equation (I), in the following way.

$$E_o = 1.02\, E_c + 23.47$$

This equation applies to the results of experiments with ½-inch normal samples. In the experiments with these samples the lowest energy of blow was in the neighborhood of 170 foot-pounds, so that an individual observation of the percentage deformation produced by a blow of 170 foot-pounds might result in a $23.47/170 \times 100 = 14 \pm$ per cent error in the estimate of the blow which produced that deformation. The greater the percentage deformation produced, the less is the chance of individual observations resulting in errors in the determination of the energy-deformation relationship from equations (I) or (II). From the above it will be clear that duplicate or, better, triplicate tests should be made, if correct values for the parameter b are desired.

This equation may be expressed logarithmically as follows:

$$\log E = \log b + (1.56—0.47 \log. b) \log. D \qquad \text{(II)}$$

Those interested in the use of this formula may employ the values shown graphically in Fig. 2. They will find, however, that some discrepancies occur between the observed and the calculated values. This is due in the main to the fact that it is somewhat difficult to plot such curves as are shown in Fig. 2 in such a way as to include satisfactorily all the values observed. A study of a large number of such curves, however, resulted in the equation shown above, by means of which a more satisfactory representation of the relationship between energy and percentage deformation is obtainable. For the sake of showing how closely these equations enable an estimate to be made of the energy required to deform normal samples, the following are submitted: (1) A ½-inch normal sample of steel, containing 0.56 per cent carbon was found to be reduced by 12.3 per cent in height as a result of a blow of 169.5 foot-pounds. By using the above formula, an estimate was made of the amount of energy that would be required to reduce this sample by 36.0 per cent in height at the same temperature. This was found to be 523.6 foot-pounds. The actual energy required to deform the sample was found to be 508.5 foot-pounds.

(2) A ½-inch normal sample of steel, containing 0.08 per cent carbon was found to be reduced by 44.0 per cent in height as a result of a blow of 169.5 foot-pounds. By using the above formula, an estimate was made of the amount of energy that would be required to reduce this sample by 71.0 per cent in height at the same temperature. This was found to be 497.7 foot-pounds. The actual energy required to deform the sample was found to be 508.5 foot-pounds.

Turning now to the tests referred to in the present paper, these were made, without exception, on 1-inch normal samples of the various steels examined. Equation (I), referred to above, was obtained as a result of a critical examination of a large number of such curves as are shown in Fig. 2. These refer to ½-inch normal samples of steel. In order that equation (I) may be applied to normal samples of all sizes, it is necessary to bear in mind Tresca's theorem, which states that the energy required to produce analogous changes of shape of geometrically similar bodies in similar physical state varies as the volumes or weights of the bodies. The law may be expressed mathematically as follows:

$$\frac{E_1}{E} = \frac{V_1}{V} \qquad \text{(III)}$$

If, now, E be the energy required to reduce the height of, say, a ½-inch normal sample of steel by D per cent, then E_1, the energy required to reduce the height of a normal sample having a volume V_1 cubic inches by the same amount, will be:

$$\frac{EV_1}{0.0982} \qquad \text{(IV)}$$

This is so because the volume of a ½-inch normal sample is 0.0982 cubic inches.

Equation (I), then, may be generalized as follows:

$$E_1 = \frac{V_1 b}{0.0982} \cdot D^{(1.56-0.47 \log b)} \qquad \text{(V)}$$

For the 1-inch normal samples referred to throughout this paper the generalized equation becomes:

$$E_1 = 8.0\, bD^{(1.56-0.47 \log b)} \qquad \text{(VI)}$$

By means of equation (VI) an estimate can be made of the amount of energy required to reduce the 0.16 per cent carbon steel referred to in Fig. 3 by 40 per cent in height under a single blow at a temperature of 950 degrees Cent. (1740 degrees Fahr.). Reference to Fig. 3 will show that this steel is reduced by 21.5 per cent in height at 950 degrees Cent. under a blow of 520 foot-pounds, this amount of energy having characterized the blows used throughout the series of experiments referred to in this paper. By using equation (VI) as suggested above, one arrives at the conclusion that 1690 foot-pounds of energy would be required to effect the deformation of 40 per cent referred to above.

Knowing the amount of energy required to reduce a 1-inch normal sample of steel by, say, 40 per cent in height, the Tresca relationship, equation (III), can, of course, be applied to estimate the energy required to reduce the height of normal samples of the same steel of other dimensions by the same amount — 40 per cent.

It is fully recognized by the author that before accurate de-

terminations can be made of the energy required to effect specific changes of shape in samples of varying dimensions, far more work than he has presented here must be done. It is believed, however, that the method here described does offer a means, rough and ready though it may be, for obtaining a very much closer idea of the energy which must be expended to effect specific changes in the shape of normal samples than has hitherto been possible.

Should information regarding the energy required to deform cylinders other than normal be needed, use may be made of the curves shown in Fig. 22 of Appendix III of the author's 1924 paper.

Acknowledgment

The author desires to acknowledge the help afforded him by Mr. J. Barbeau, who under the author's direction carried out practically all the forging experiments described above, and by Mr. Desmond Hunter, who analyzed the steels investigated, and the encouragement given to him in this work by Dr. H. B. Speakman, director of the Ontario Research Foundation.

DISCUSSION

Written Discussion: By H. H. Ashdown, metallurgist, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

I know of no paper to which I have submitted a discussion which has given me greater pleasure than this paper by Mr. Ellis. I have known for many years the thoroughness of the author's work, and its value is greatly enhanced by his close cooperation with works problems.

There is tremendous significance in the opening paragraphs of this paper directing attention to the resistance to plastic deformation of steel by dynamic force when passing through its critical range, and I hope this will receive greater attention of the forge and mill executives than has the work of Robin.

What Mr. Ellis has unquestionably proved in his experimental and research work has been my own experience in forging great masses of steel under the forging press and smaller volumes under steam hammers. He also has shown the marked difference in increasing hardness at the same temperature, as the carbon percentage increases, and also the hardening effect of the presence of alloys at elevated temperatures. I believe he would find a marked increase in hardness in the forgeability of steel with increasing molybdenum content up to at least 0.5 per cent either in the presence of or without other alloying elements.

It is known by all forge men that, as the carbon increases, the steels are harder to work right through the forging range and they are known as hard quality steels. More particularly is this noticeable when approaching and working through the critical range, which never should be done with carbon

steels above 0.30 per cent carbon or any alloy steel, particularly with forgings of large dimensions.

Mr. Ellis has called attention to the marked hardening effect of the presence of nickel on the forgeability. This again is very noticeable in practice, particularly so in the lower temperature ranges, where, unsuspectingly, considerable damage is done to the steel.

In discussing a paper before the British Iron and Steel Institute in 1917, I there called attention to the fatal mistake of "cold working." Particularly is this the case at the ends of forgings where the material loses heat quickest and which usually is the last portion to be worked. The forge man tries to get the very most out of his heat in place of reheating the ends for a short period. If one watches the ends of forgings being "cold-worked," around or through the critical range, he will notice bright diagonal lines appear which may be due to local generation of heat resulting from a shearing of the crystalline structure in those areas, or the evolution of heat resulting from the physical changes taking place in the critical range. Under these conditions, is it surprising that forgings tested transversally give a 45 degree fracture, the fractures being those of two faces having been rubbed together? I have known of hollow forgings, each worth $10,000, being scrapped from this cause, and yet when 12 inches of material was cut away and further tests taken, the results have shown the material was all that could be desired.

Again, in discussing a paper by Blankenship on forging practice at the Chicago Convention in 1930, I called attention to the risk of serious injury to the steel when forging through and below the critical ranges.

The indication of this increasing hardness can be distinctly felt under the hammer by the increasing solidity of the blow, and under the forge press, the indication is shown on the pressure gage by the increased pressure for the same volume displacement. A further indication, when making hollow forgings, is the grunt on the mandrel due to the biting action of the hardening surface. It may be true that semi-cold working may raise the elastic limit and yield point, but this, as has already been shown, is done at the risk of irreparable damage in other directions. The internal stresses set up in the steel are such as to often cause internal clinks if the forgings are allowed to cool normally after forging.

There is yet another viewpoint to "cold forging." That is the effect on the forging equipment. It weakens the foundation, causes broken hammer rods and legs, and it is not uncommon, due to overstressing, to see a loose column in a forging press.

Mr. Ellis directs attention to the difference in forgeability sometimes to be observed in two different supplies of steel of precisely the same analysis. It has been my experience that a dirty steel compared with a clean steel of the same analysis forges more readily, and again, a basic open-hearth steel is noticeably easier to forge than an acid open-hearth steel of the same analysis.

It is sometimes stated that papers emanating from University sources are too "high-brow," but I suggest that this paper and others before this session, if read and compared with conditions in practice, offer high potential commercial value, or, in other words, are "dollar papers." With this object in

view, I have endeavored to indicate some of those dollar saving directions.

I have touched on but few of the valuable points of information in this paper, but have pleasure in expressing my personal indebtedness to Mr. Ellis for the store of information disclosed.

Written Discussion: By N. L. Deuble, department of metallurgy, Republic Steel Corp., Central Alloy Division, Massillon, Ohio.

Mr. Ellis has performed a very nice piece of technical work in determining the percentage of compression produced on various carbon and alloy steels with a single blow. His paper indicates that a great deal of thought had been given his subject prior to carrying out his experiments.

Everyone is undoubtedly familiar with the fact that increased carbon content decreases plasticity, but they are not familiar with the rapidity with which it decreases. The effect of the various alloys is not known, except that in general it is felt that they increase slightly the energy necessary to produce a definite deformation.

The curves drawn by Mr. Ellis from his data give the forge man a general guide to the energy required to reduce the various steels in forging. It would be rather difficult to interpolate from his figures, the energy necessary to forge a steering knuckle or some other complicated drop forging where a great many blows are necessary. The curves set forth also indicate that steel is less plastic as it nears the critical range. This also is generally known.

In this experiment it would have been advisable, in all cases, to have started from hot-rolled material because the curves below the critical points would have been more comparable. Comparing the curves for steels "I" and "J," it will be noted that one offers considerably more resistance than the other. The Brinell hardnesses indicate that "I" was probably hot-rolled, while "J" was annealed. Undoubtedly the "I" steel was harder after normalizing, as it is slightly higher in carbon and has the addition of vanadium—this would be expected. However, it would not necessarily follow that the resistance to deformation would be increased to such a great extent if the steels were of the same hardness originally.

In comparing heats of similar analysis, but manufactured under different practices, Mr. Ellis finds practically no difference. In actual practice this is not true, for there have been cases of S.A.E. 5150 steel where the forge shop hammerman could distinguish between two sources of supply by the flow of the material under the hammer. In one case the steel required three to four extra blows to bring it down to size, the same forging temperature being used in both cases. It may be that the 520 foot-pounds blow on one inch square samples is too severe to bring out these variations, but in view of the curves on carbon steels, this is hard to believe.

From a technical point of view, this paper is exceedingly interesting and indicates that considerable thought and care were exercised in the experimental work. However, to practically apply this data to every day drop forgings would be exceedingly difficult: first, because of the intricate shapes of drop forgings; second, because of the large number of blows required to fill out the average forgings; third, because of the rapidly falling temperatures, due to very thin sections in contact with relatively cold dies; fourth, because of

the tendency of some alloy steels to work-harden, especially when worked near the critical points.

Written Discussion: By John P. Fleming, forge supt., Alco Products, Inc., Dunkirk, N. Y.

We have read the interesting paper by Mr. Ellis on the forgeability of steel. We agree with the author that carbon is by far the most potent in its effect upon malleability as compared with the elements nickel, chromium or vanadium.

The curves showing the malleability of the various steels as influenced by temperature are interesting and are a valuable addition to the forgeman's knowledge regarding the temperature which should be used on these steels to permit deformation to take place with the least expenditure of power.

We should like to ask Mr. Ellis if the samples used in his experiments were cut from bars as rolled; or were they machined to size? A variation in diameter which is usual in a rolled bar may account partly for the difference in the malleability of these steels.

The addition of nickel, chromium and vanadium to medium carbon steels as shown by the author produces some change in forgeability. That vanadium alters the rate of change in forgeability with temperature and offers greater resistance to deformation at the lower forging temperatures we believe to be correct. At elevated temperatures (above 2000 degrees Fahr.) the influence of vanadium produces no effect on the malleability of medium carbon steels.

The author is to be congratulated on the excellent curves brought out in his experiments, the position of the various critical points being of particular interest.

Written Discussion: By Adam M. Steever, chief metallurgist, Great Lakes Forge Co., Chicago.

The author's paper is of particular interest to the manufacturers of drop forgings and he has given us a wealth of information on the forgeability of steel. The average commercial forge shop produces a large percentage of alloy steel forgings, especially those of the S.A.E. specification. In forging the medium carbon-nickel, nickel-chromium, and chromium steels a greater amount of energy must be applied to the materials undergoing deformation than the low carbon alloys or plain carbon steels. Nickel and chromium decreasing the forgeability of medium carbon steels as demonstrated by the author has a very important influence upon the life of impressions in drop forging dies. These materials require either additional energy in the form of larger forging equipment or increased blows from forging equipment that would satisfactorily produce the same part if made from plain medium or low carbon steels. In either of the above mentioned an enormous reduction in die life is experienced in forging these materials.

The information presented by Mr. Ellis will be valuable to the drop forger in estimating the approximate die life which can be expected and will aid in the selection of the size of hammer required for certain alloy steels. His outlined methods offer a means of obtaining the above data more accurately than any data heretofore developed.

Written Discussion: By Henry B. Allen, metallurgist, Henry Disston and Sons Co., Tacony, Philadelphia.

The forgeability of steel is, of course, an important consideration both to the steel user and in the steel mill. The maker of drop forgings is vitally concerned with die life. While a more difficultly forged steel can be made softer by increasing its temperature, this modification in practice entails other disadvantages. The steel maker is concerned in much the same way. A low hammering and rolling temperature decreases mill costs and reduces the possibility of excessive surface decarburization. A better understanding of the effects of composition on the hot working of metals cannot therefore be without real value.

Mr. Ellis' studies possess the decided attraction of covering one of the lesser explored fields in metallurgy. One immediately wants to attempt the correlation of the newly reported facts with other data, both laboratory and practical. One interesting comparison would be with published tests on the hot tensile strengths of similar steels.

The writer has been told by an experienced steel roller that the softness with which a low carbon steel will roll can be vitally affected by the temperature and treatment the ingot receives in hammer cogging. Whether this difference will persist in the finished bar and later show in reforging a 1-inch round is not known, but it would be supposed that the effect might persist, although to much less degree. A similar softening effect is observed in working down high carbon steels made with less scrap in the furnace charge. In this connection, Mr. Ellis shows by his forgeability test, which he has been kind enough to make for the writer and which is reported in this paper, that but little difference remains in the steel after rolling down to 1-inch round bars. A slight difference does show, however, and it is consistently in the right direction to confirm the greater differences observed in the steel mill. Mr. Ellis has kindly consented to make further tests using specimens taken from the steels when at an earlier stage of fabrication.

Because other factors besides chemical composition of the steel will have their effect upon its forgeability it is hoped that Mr. Ellis will continue his work taking into consideration the previous history of the steels. A valuable addition to the present paper would be the complete analyses of the steels used. The difference in forgeability at 1000 degrees Cent. between the 0.10 and 0.16 per cent carbon steels is so comparatively large for the small difference in carbon content that a complete analysis would be especially welcome.

A continuance of forgeability tests to include the higher chromium steels and high speed tool steels would be of particular interest to tool steel makers and users, especially if extended to temperatures around 1200 degrees Cent.

Written Discussion: By F. W. Spencer, Coventry, England.

I was interested in reading this paper by Mr. Ellis. It represents a considerable amount of work upon the author's part.

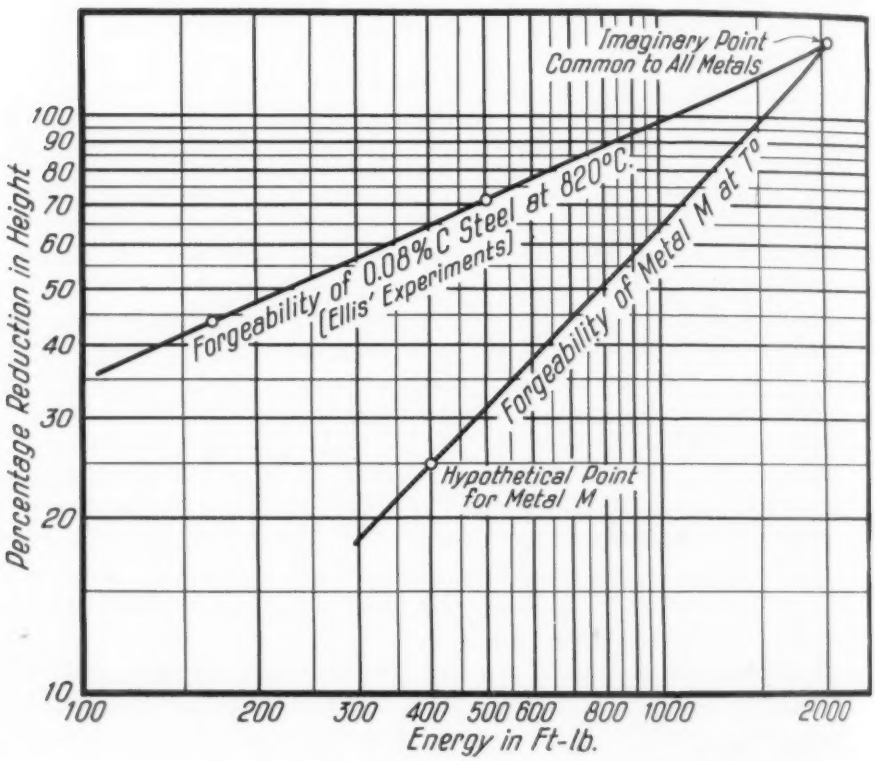
No mention, however, is made of the condition of the anvil or pallet faces of the drop hammer. I presume that these were hardened and ground perfectly smooth and flat. This is important, as I have found, when making comparison tests between the blow of a 1000-pound drop hammer and a fric-

tion screw press, that the condition of the surface of the pallet faces affects the results considerably.

The practical forge man would like a simple formula for finding out the size of hammer forging machine or press required to deform, flatten, or upset certain common shapes. This will require time and expense on someone's part, and the makers of forging equipment have a splendid opportunity for carrying out useful experiments in this direction.

Written Discussion: By S. A. Main, Sheffield, England.

It may be of interest to know that the useful formula given by Mr. Ellis



Graph on Log-Log Coordinates, Where Relation Between Energy of Blow and Reduction of Normal ½-In. Sample Plots as a Straight Line.

in his paper on the forgeability of steel can be put into a form enabling its rapid working by graphic methods. His formula, which gives the energy required for stated amounts of deformation of a steel cylinder, is

$$\log E = \log b + (1.56 - 0.47 \log b) \log D$$

The parameter b is clearly the value of the energy E for a reduction D of 1 per cent. The formula can be rewritten

$$3.32 - \log E = a\ (2.13 - \log D)$$

where a, the parameter chosen in this equation, is equal to $(1.56 - 0.47 \log b)$. In the imaginary condition when $\log D = 2.13$ (corresponding to a reduction of 134.9 %), $\log E$ is 3.32 ($E = 2089$ ft-lb.) whatever the value of a, for then the right side of the second equation vanishes and $\log E$ becomes equal to 3.32. That means that under these conditions all materials coming within the formula at all temperatures would behave alike.

These conditions can only exist in a mathematical sense, but this fact assists the plotting, for on double logarithmic paper, E and D give a straight line, the slope of which is the parameter a.

All such lines for all materials and for all temperatures covered by the formula pass, when produced beyond the $D = 100$ per cent line, through the point $D = 134.9$, $E = 2089$ foot-pounds. This is shown on the accompanying diagram. It follows that all that is necessary to determine the forgeability of a normal sample of steel at a given temperature is to join up any single accurate observation with this point by a straight line, which shows all corresponding values of deformation and energy for that particular steel and temperature.

The divergence downwards of such lines indicates that when the behavior of any steel at any temperature is being compared with that of the same or any other steel, at the same or any other temperature, the ratio of difference becomes less the larger the amount of deformation on which the comparison is based.

The same limits of applicability naturally apply to the modified formula, and to the plotting, as to the original formula.

It may be of further interest to know that, according to my own observations at the Hecla Works of Hadfields, Ltd., a formula of the same general form applies approximately in the case of copper cylinders tested cold.

Author's Closure

In dealing with the written discussions of my paper, it may be well for me to consider them in alphabetical order. For this reason I will take up first the contribution which Dr. Allen has forwarded.

I am particularly interested in his remarks regarding the increased forgeability which can result from variations in treatment of the ingot during hammer cogging, and the similar softening effect that is observed in working down high carbon steels made with less scrap in the furnace charge. Dr. Allen points out that I have been unable to show clearly by my forgeability tests that any marked difference remains in steels of eutectoid analysis, despite variations in methods of manufacture and in the character of the charge. Dr. Allen points out, however, that the work described in this paper does support the view that such a difference may exist, and I am happy to think that I may be able to cooperate still further with Dr. Allen in this connection. Dr. Allen's suggestion that a valuable addition to the present paper would be the complete analyses of the steels used will, I believe, be complied with at a later time.

It is not at all improbable that I will carry this work forward to include the higher chromium and high speed tool steels.

I much appreciate the remarks which have been made by Mr. Ashdown, whose wide experience in the manufacture of heavy forgings apparently falls in line in the main with the results which I have presented in this paper. I am fully in agreement with Mr. Ashdown's remarks regarding the importance of the effect of the critical range upon the forgeability of steel. Anyone who studies the curves shown in the paper cannot but be impressed by the immense reduction in plasticity which occurs when the A_3 point has been passed.

In reply to Mr. Deuble's suggestion that it would have been advisable to have started from hot-rolled material, it may be said that all the steels, with the exception of the eutectoid steels referred to in the section on the influence of melting practice and the eutectoid steel of which the malleability-temperature relationship is shown in figure 3, were tested in the hot-rolled condition; in other words, only the eutectoid steels were in the annealed state prior to forging. The 0.68 per cent carbon steel of Fig. 3 was tested in the "as-rolled" condition, the 0.85 per cent carbon steel in the annealed state. In that connection it may be of interest to mention the results of experiments made on the steels I and J, which were the subject of Mr. Deuble's discussion. Samples of these steels were heated in a Globar furnace, passing the A_3 point approximately 35 minutes after introduction into the furnace, and reaching the temperature of 860 degrees Cent. 1 hour later. The current was then shut off and the samples allowed to cool with the furnace. When forged at approximately 720 degrees Cent., steel I was reduced 9.1 per cent, and steel J 9.7 per cent; when forged at approximately 740 degrees Cent., steel I was reduced 9.8 per cent, and steel J 9.2 per cent; when forged at approximately 955 degrees Cent., steel I was reduced 9.6 per cent, and steel J 9.4 per cent. To all intents and purposes, then, the two steels after annealing were equally amenable to plastic deformation at temperatures below the critical range. In brief, annealing wipes out the effects of vanadium on the forgeability of steel of this composition at temperatures below the A_1 point.

Mr. Deuble raises the point referred to by Dr. Allen regarding the effect of analysis upon the forgeability of steel. It is not my wish to suggest that steel made by, shall we say, the acid Bessemer process would be similar in its resistance to forging to steel made by the basic open-hearth process. All that I have attempted to point out in this paper is that, when dealing with a particular series of eutectoid steels which had been produced from charges varying quite considerably in character, no differences in malleability worthy of note were encountered. I would be the last to support the view that methods of manufacture were unimportant in this connection and should be glad to have the opportunity of testing steels of similar chemical analysis (using the term "chemical analysis" in the orthodox sense), but of different origin (using the term "origin" in the widest sense).

I agree with Mr. Deuble that it would be difficult to apply the results of my work directly to the manufacture of drop forgings at the present time. I hope later, however, to discover how variations in shape of the sample, etc., affect the amount of energy required to reduce the material and ultimately to present to the metallurgical industry information which will assist them to

determine beforehand what energy is required to form a piece of steel of any given analysis into a particular shape.

Mr. Fleming's kind remarks are greatly appreciated. Mr. Fleming asks whether the samples used in these experiments were cut from bars as rolled or were machined to size. They were cut from bars as rolled and were carefully machined on the cut surfaces before testing so that such variations in height were negligible. It may be taken as correct, also, that variations in diameter were inappreciable.

It is interesting to note that Mr. Fleming believes vanadium to alter the rate of change of forgeability with temperature.

Mr. Steever's remarks bring out a point which had scarcely been considered by me when my experiments were under way, a point which has been referred to by other contributors to this discussion—namely, the importance of forgeability upon the life of the dies used in forging. If any work that I have conducted to date will lead to an improvement in the life of dies, I shall certainly be well satisfied.

In reply to Mr. Spencer's comments, it may be stated that both anvil and hammer were hardened, their faces being ground prior to use. Care was taken to have the surfaces of the anvil and hammer parallel to one another in the machine.

It is the hope of the author to be able to gather information regarding the effects of variations in the shape of parts being forged and the energy required to deform them by definite amounts. Some interesting relationships have already been obtained with cones and frustra of cones.

Mr. Main's observations are of particular value, since they bring out so clearly the significance of the equation and, particularly, to the parameter b. The fact that a formula of the same general form applies approximately in the case of copper cylinders tested cold is of considerable interest.

In concluding my remarks, I would say that I should appreciate any suggestions that members might give me regarding future work in this connection.

METALLURGICAL SPECTRUM ANALYSIS

By Welton J. Crook

Abstract

This paper describes the construction and use of a 21-foot focal length grating spectrograph as applied to metallurgical analysis. A new method of reading is described, in which the spectrum film is placed in an enlarger and projected onto visual charts. The readings are made at a magnification such that 1 Å. U. = 5 millimeters. In this way the tedious method of the use of a micro comparator is obviated.

Introduction

FOR a number of years the spectrograph has been made use of as an adjunct to chemical methods of analysis, but it seems that the method has been applied, except in certain cases, mostly by the scientist rather than by the technologist. It is believed that most workers in the engineering and metallurgical fields have felt that the method was too intricate, slow and cumbersome so that it scarcely had a place in the ordinary well-equipped metallurgical laboratory. During the last five years or so, articles have occasionally appeared in the technical literature, calling attention to the advantages of spectrographic methods, and some texts on metallurgical analysis have devoted numerous pages to spectrographic technique. Naish and Clennell[1] devoted a chapter of eighteen pages to this subject, and include an excellent working bibliography. The instruments described are restricted to the prism types, but the general discussion can be applied equally well to grating instruments.

The gradual recognition of the method is shown by the increasing number of articles appearing in technical and trade magazines. Numerous applications are described for special purposes such as in metal refining and in the steel industry. G. Scheibe[2] points out

[1]W. A. Naish and J. E. Clennell, "Select Methods of Metallurgical Analysis," John Wiley and Sons, New York.

[2]G. H. H. Konzern, "Mitteilungen aus den Forschungsanstalten," July, 1931. Abstracted in *Iron Age*, April 7, 1932.

The author, Welton J. Crook, is a member of the society and is professor of metallurgy, Stanford University, California. Manuscript received November 22, 1932.

several salient features in connection with the application of spectrometry to metallurgical analysis. He states that the advantages of the method, when applied to steel analysis, consist in "high sensitivity, freedom from hindrance of one chemical element with the determination of another, speed and smallness of sample so that a finished piece may be analyzed without injury, low cost, and the permanent documentary evidence of spectrograms."

When general metallurgical analysis and investigation are considered, the outstanding advantage of the method is the ease with which preliminary quantitative metal analyses may be secured, when dealing with complex alloys, on which a plan of chemical quantitative analysis may be based; also the great ease and speed with which the composition of steels and other alloys may be compared. In the realm of mineral analysis, especially where the rarer elements are encountered, the spectrograph is almost indispensable.

Much work has been done and continues to be done on the subject of quantitative spectrographic analysis, particularly in connection with the estimation of small quantities of impurities in refined metals. It is believed that quantitative spectrum analysis has its best field along these lines, although some workers, particularly in Germany, believe that within a few years the spectrograph will entirely supplant the chemical laboratory in industrial applications. Others, well skilled in the art, agree with the writer that the spectrograph is only a most useful adjunct to chemical methods.

In general, when quantitative measurements of any degree of exactness are undertaken, the apparatus and operations must be greatly complicated except, perhaps, in one method described by Meggers, Kiess, and Stimson[3] and others in which small quantities of impurities in refined metals may be estimated by the comparison of spectra from standards of known impurity content.

Several years ago the need for spectrographic equipment was felt in the various divisions of the Department of Mining Engineering at Stanford University. Some preliminary study was made regarding the best type of equipment for the needs, as well as to the minimum cost at which suitable apparatus could be secured. Adequate equipment of the usual type, which could be purchased from instrument manufacturers, was found to be beyond the funds available; also, the usual methods of reading the spectrograms in general

[3] W. F. Meggers, C. C. Kiess, F. J. Stimson, "Practical Spectrographic Analysis," U. S. Bureau of Standards Scientific Paper No. 444, July 1921, p. 244-252.

use were considered to be time consuming and cumbersome. This paper describes the apparatus finally installed and the methods of operation evolved. It is hoped that the information given may be of use to others and may help, in a small way, to extend the use of spectrometry in metallurgical investigation. The author is an engineer and approaches, with trepidation, the discussion of a matter which up to the present time has resided largely in the realms of the physicist and scientist. No basal knowledge of the science of spectrometry is possessed or assumed. Interest is limited to the application of the spectrograph as a useful tool in aiding metallurgical investigation. Nevertheless, no one can work long with a spectrograph without becoming fascinated and enthusiastic with its possibilities. This is shown in the writings of many authors of which Jacques Bardet[4] and G. Urban are examples. "Index of Spectra," by the late W. Marshall Watts, Ismalia, Clatterton Gardens, West Cliff on Sea, Essex, England, consists of 16 volumes. The latest, Appendix AA, was issued in 1931. Each volume contains complete tables of spectrum lines of one or more elements, and generally records the results of several workers with bibliography.

"The International Critical Tables," Vol V, is a most useful reference containing a fairly complete list of the lines of all the elements. It is almost indispensable to those working in spectrography.

Many excellent technical publications, catalogs, and descriptive circulars have been issued by a number of optical manufacturers such as Adam Hilger, Ltd., London; Carl Zeiss, Jena; and Bausch and Lomb Optical Company, Rochester, New York. These publications deal almost entirely with instruments of the prism type.

Choice of Equipment

It should be stated at the outset that if serious and useful work is to be undertaken with the spectrograph, an instrument, either of the prism or grating type, having a reasonably large dispersion must be available. The small glass prism instruments sometimes seen in chemical laboratories are merely scientific toys. Use of such apparatus leads to discouragement and prejudices the mind of the operator against spectrographic methods.

Without undertaking a long discussion of the various merits of

[4]Jacques Bardet, "Atlas de Spectres d'Arc," 1926, Gaston Dorin et Cie, Editeurs, 8 Place de l'Odion 8, Paris.

the several kinds of available instruments, it may be said that before installing the equipment described in this article, some study was made and consideration given to the matter. It was desired to obtain an instrument of maximum dispersion and ease of operation consistent with the relatively small amount of money available for the purpose. Final choice was made on a grating spectrograph having a focal length of 21 feet. An instrument of this type has great dispersion power, freedom from optical accessories, and desirable ease of manipulation. It has several admitted disadvantages, chief of which is the difficulty of obtaining a grating of suitable size.

Large gratings are obtainable from only a few sources: from two universities in the United States and one source in England. The instrument requires a relatively large space for installation and cannot be purchased ready to operate, but must be built. The results obtained so far have justified, at least in our minds, the original decision. One great advantage of the grating over the prism is the constant dispersion over the whole spectrum as compared with the great crowding of the prism spectrum toward the visible end. This point will be particularly appreciated later when the methods of reading spectra are discussed.

Description of the Apparatus

The essential components of the grating spectrograph are the grating, activating apparatus, collimating lens, mechanical slit, casette or photographic film holder, and the arrangements for maintaining the casette in proper alignment and distance from the grating. The grating used is of the concave type having a focal length of 20.71 feet, and is ruled for a length of 6 inches with 14,600 lines per inch. It was obtained from the laboratory of Professor Woods at Johns Hopkins University. In order to be in proper adjustment, the grating, slit, and casette must be maintained in a certain exact relationship to each other. Adjustment will be maintained if the grating, slit, and casette are placed on the circumference of a circle whose radius is one-half that of the radius of curvature of the grating. This relationship is shown in Fig. 1. R is the radius of curvature of the grating. GCS is a circle whose radius r is one-half R. The conditions are fulfilled if the grating G, the slit S, and the casette C lie on the circumference of the circle whose radius is r. In the particular grating used, R is 20.71 feet, so that r equals 20.71 divided by 2 feet.

The spectrum is in focus on the arc of the circle SCG. In order to simplify the mount and make a setup which may be readily adjusted,

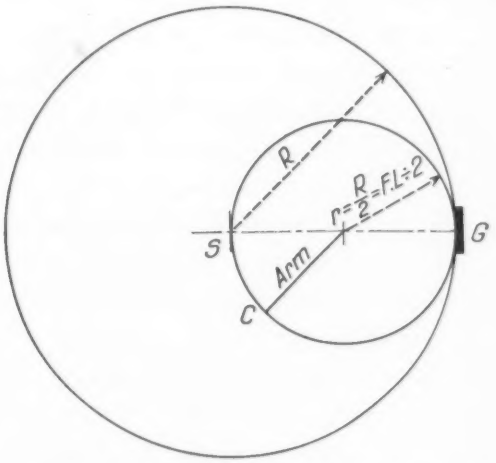


Fig. 1—Diagram Showing Method of Mounting Grating.

a strong hub was set up at point H and connected with the casette by a truss arm, marked "arm" in Fig. 1.

A number of methods of mounting the grating spectrograph

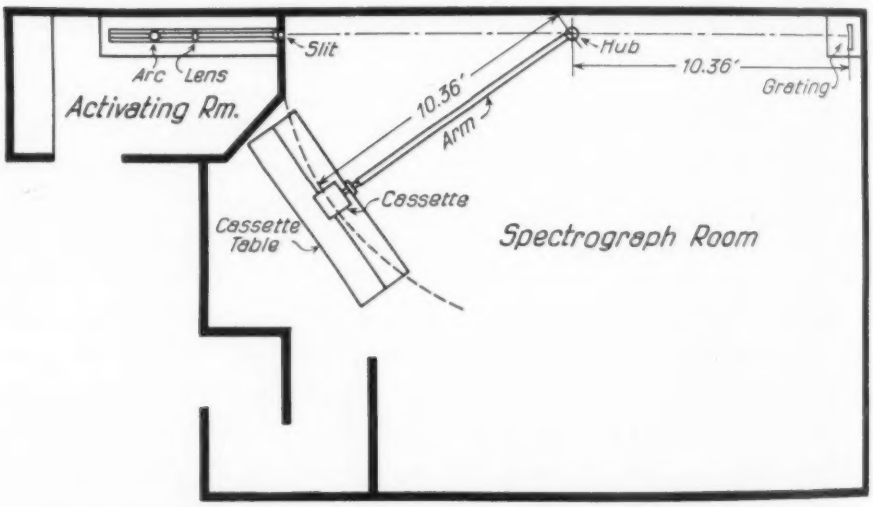


Fig. 2—Spectrographic Equipment Setup.

have been suggested and used since Roland developed his original mount. Most of these methods involve very accurate and intricate machine work which was beyond our capabilities. Fig. 2 shows diagrammatically the type of mount which was evolved in our laboratory and which has given good satisfaction. The setup requires

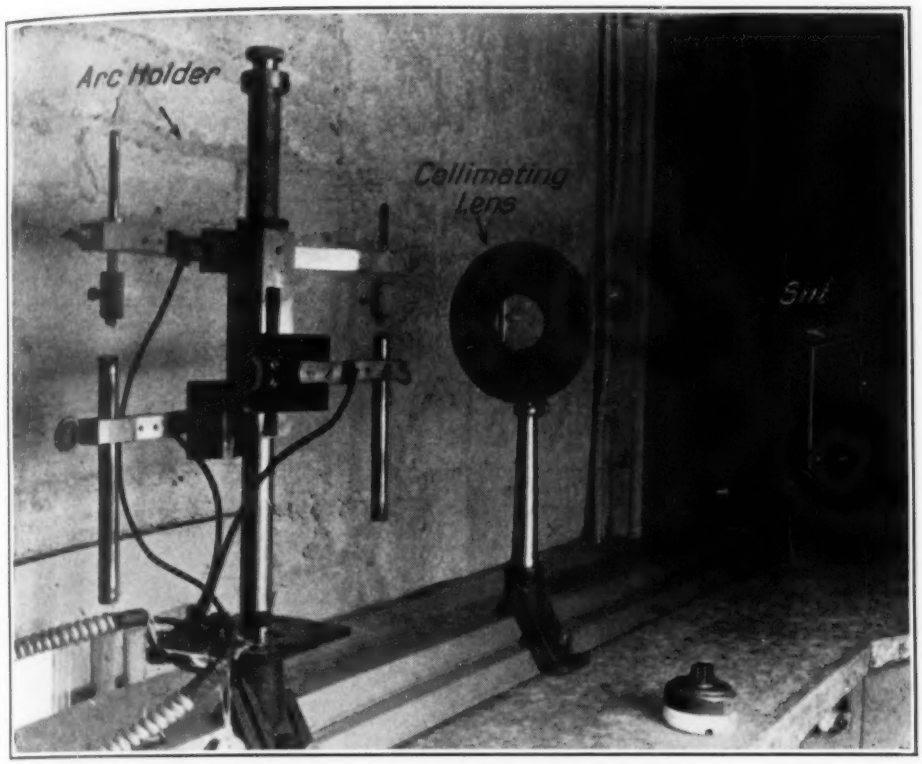


Fig. 3—Arrangement of Activating Room.

two separate rooms. One small room, marked "activating room," contains an optical bench upon which is mounted a double adjustable electrode holder, a quartz collimating lens and the slit. The arc is connected, through an adjustable carbon disk resistance, to a source of 220-volt direct current, and the circuit includes a suitable ammeter. The slit is mounted on a stand which rests on the optical bench and is fitted to a connection through the light-tight partition separating the activating room from the spectrograph room proper. This latter room must be capable of being made absolutely light tight, and it is a convenience to have a photographic dark room directly connected to it. An electrically controlled solenoid shutter is placed in the spectrograph room in front of the slit opening, and is controlled by a switch in the activating room. A red lamp globe is included in the shutter circuit and indicates when the shutter is open or closed.

The arrangement of the activating room is shown in Fig. 3. The grating with its adjustable mount is placed on a heavy steel plate which is very firmly attached to the corner of the stone building.

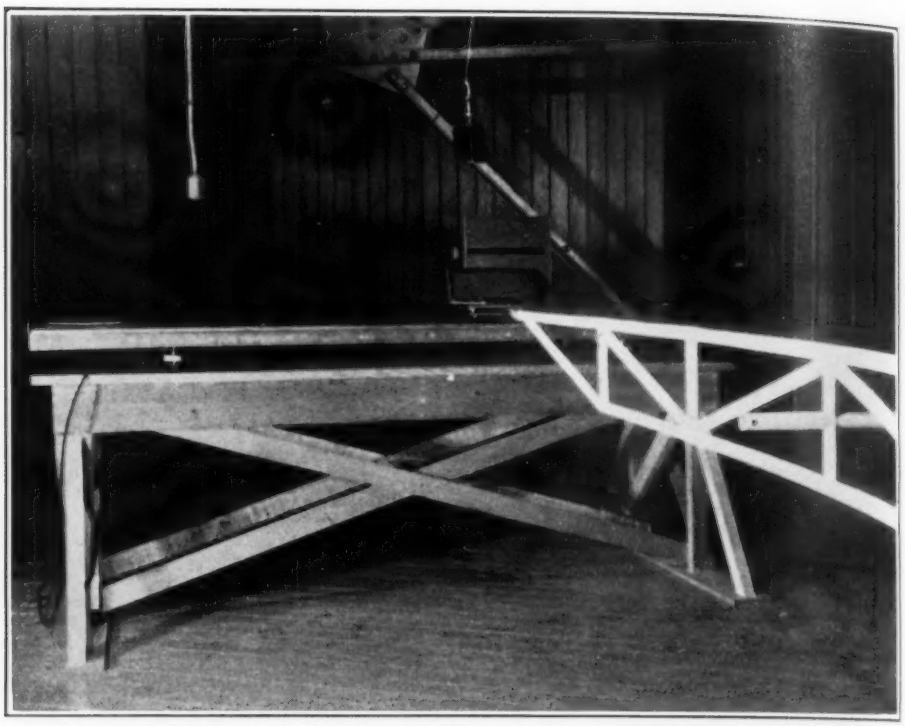


Fig. 4—Cassette Table with Cassette and Film Holder.

The face of the grating is placed 20.71 feet from the slit. Halfway between the grating and the slit another steel plate is attached to the wall supporting a strong vertical hub. This hub carries a truss arm, constructed of brazed steel tubing, at the end of which is attached the casette. Fig. 5.

The casette itself is mounted on adjustable steel plates fitted with two large ball bearings which run on a steel plate attached to the table top. A general view of the casette table is shown in Fig. 4.

The adjustment of the whole apparatus is made as follows: Having lighted the arc, the collimating lens is adjusted so that the arc image is in focus and exactly centered on the slit. The slit is then opened to allow a strong beam of light to strike on the grating. A surveyor's transit or level is then set up in the spectrograph room at a position so that the instrument may be traversed to view the grating, slit opening and the casette. The horizontal center of the grating is then adjusted to the same level as the center of the slit opening, and the opening in the casette is adjusted in a similar manner. The optical center of the grating, which appears as a bright image of the slit, is then directed back on the slit opening by means of the



Fig. 5—Closeup View of Casette.

levelling screws on the grating mount. Then, with the room in darkness, the casette having been moved to the visible region of the first order spectrum, the exact center of the spectrum band is adjusted to the casette opening. The instrument should then be in adjustment and with ordinary care will stay in this condition indefinitely.

Operation of Equipment

In arc spectrum work several kinds of electrodes are in common use. These include rods of the metal under examination, purified carbon electrodes, rods of copper or silver, and iron electrodes. For general purposes, the writer has found that iron electrodes arranged in the form of the "Pfund arc" are the most convenient; but

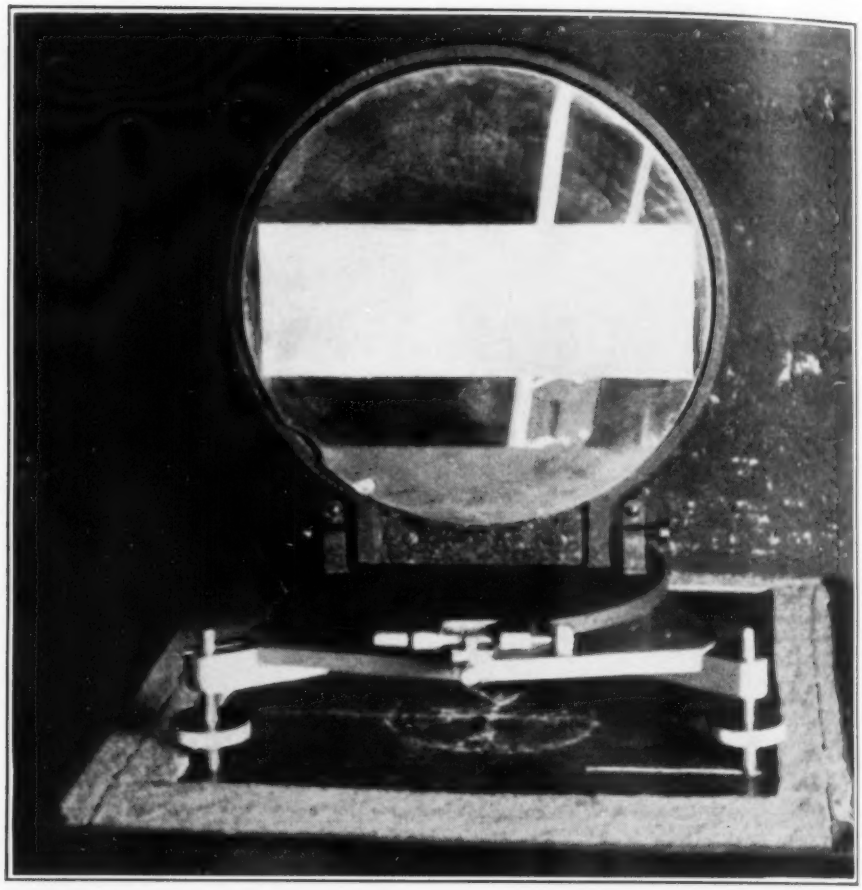


Fig. 6—Closeup View of Grating.

it must be noted that unless an instrument having great dispersion power is used, the superimposition of the crowded iron spectrum which occurs will obliterate very thoroughly the spectrum of the material under examination. With the 21-foot grating this condition gives no trouble.

The Pfund arc used consists of two electrodes of Armco iron, the upper having a diameter of about ¼ inch and the lower about ½ inch. The lower and positive electrode is drilled with a shallow depression about ⅛ inch deep. The upper electrode is fitted with an adjustable brass sleeve or radiator which prevents the iron from melting too rapidly and forming too large an oxide bead. The details of the electrodes are shown in Fig. 3. A direct current of 5 amperes at 220 volts has been found to be the most convenient. When carbon electrodes are used, a similar procedure is followed

except that the positive electrode may be somewhat smaller and the radiator or sleeve is eliminated from the upper electrode. Although the carbon arc has the advantage of a more brilliant light and therefore shorter exposure times, it possesses the very great objection of producing band spectra of carbon oxide. These band spectra are particularly objectionable in the visible spectrum, and extend down into the violet. The presence of these bands, which entirely block out certain sections of the spectrum, is one of the reasons why the writer has confined his work to the ultra violet region between about 2500 and 4200 Å. U. The appearance of these band spectra is illustrated in Fig. 7, in which the spectrum of iron is below and that of the carbon arc is above. The region shown is about 3850 Å. U. Another disadvantage of the carbon arc is the rapid burning of the electrodes which necessitates continual adjustment of the arc length.

When metal specimens are under investigation, the samples are most convenient in the form of small drillings or chips. A small quantity is placed in the cup of the lower electrode of the Pfund arc and an arc struck. The sample quickly melts down to a bead. In the case of iron or steel samples, the bead almost instantly becomes oxidized to iron oxide. An oxide bead then forms on the upper electrode so that, with ferrous samples, the arc is really maintained between two iron oxide beads rather than between two metal electrodes. When hot, the iron oxide is an excellent conductor, and a very steady arc is maintained with a current of 5 amperes. Another advantage of the Pfund arc is that when an exposure is finished, the metal bead on the lower electrode may be removed with a forceps and another sample substituted. The bead does not stick to the electrode or contaminate it. Where nonconducting materials have to be examined, a portion of the sample may be ground in a clean agate mortar with a proportion of pure iron oxide. The resulting mixture is then placed on the lower electrode. When the arc is struck, generally by connecting the two electrodes for an instant with a carbon rod, an oxide bead is formed which dissolves the sample.

It is possible that this use of an oxide bead mixture has an advantage in preventing rapid exhaustion of the elements in the sample because most substances are rapidly oxidized in the presence of molten iron oxide and the oxides are, in general, less volatile than the elements themselves. In the case of the carbon arc, there is a considerable reducing effect which tends to prevent oxide formation and even reduces some oxides which may be present. The matter of

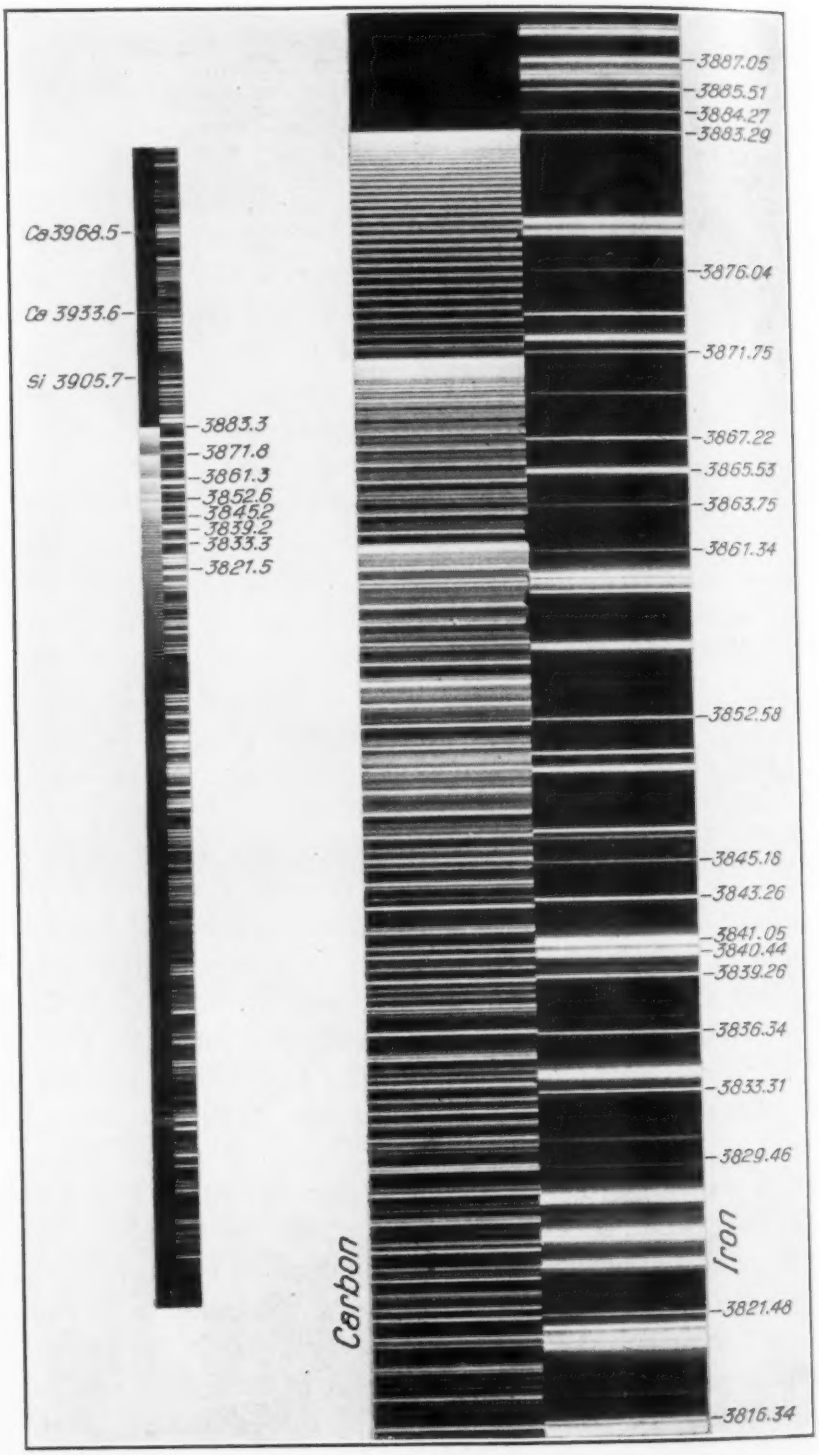


Fig. 7—Continuous Carbon Spectrum Reduced to 2/3 Original Size.

the relative exhaustion of elements in a sample treated by the two methods is under investigation at the present time; therefore a definite opinion on the matter cannot be expressed. When any form of quantitative work is attempted, the matter of exhaustion must be taken into consideration, and it is of importance even when qualitative results are desired. From tests which have been made it is believed that noticeable exhaustion does not occur in the elements ordinarily occurring in steels and common alloys. In this connection a test was made on U. S. Bureau of Standards sample No. 32A, chromium-nickel steel. The portion of the spectrum examined was between 2700 and 3340 Å. U. After the bead had properly formed, a five-minute exposure was given. This was repeated four times on the same bead, so that the total time of arc action was over 30 minutes when the last spectrogram was made. A careful check on the lines appearing in the first and last photographs showed the same number of lines of both chromium and nickel to be present. It is believed that all elements will not show the same stability. Vanadium has given no trouble in this regard. Little difficulty has been encountered from this source in most metallurgical work.

When work is contemplated in the ultra violet region it is imperative that a quartz collimating lens be used. The arc stand should be set at such a distance from the slit that when the arc image is focused on it by the lens, the image of the actual space between the electrodes more than covers the slit length. If the arc stand is too close to the slit, the production of a suitable arc length will necessitate the maintenance of too wide an electrode distance.

The mechanical slit used is fitted with an index drum calibrated so that each of the ten numbered divisions represents a slit opening of 0.001 inch. Each of the numbered divisions is again subdivided into ten. Where a slit opening of "one" is stated, an actual opening of 1/1000 inch is represented; an opening of 2 is 2/1000 inch, and so on. The slit has also been fitted with a V-shaped diaphragm which controls the vertical length of the slit opening. The choice of slit opening is of importance. Upon it depends the resolving power or ability to separate closely adjacent spectrum lines. Also, it controls the exposure necessary for photographing the spectrum because the amount of light admitted to the grating is proportional to the slit opening. It would seem that the smallest slit opening, consistent with reasonable exposure time, should be used. With the instrument used, careful microscopic study of the actual visible spectrum

showed that with a slit opening up to 3/1000 inch, lines separated by probably only a few hundredths of an Ångstrom unit can be differentiated. With an opening of 4/1000 inch, they appeared as one line.

As previously stated, the exposure required varies inversely as the slit opening. If the exposure required with an opening of "1" is one minute, a slit of "2" will require one-half minute, and so on. The exposure also varies with the particular region of the spectrum photographed, as well as with the speed and sensitivity of the plates or films used. In the visible spectrum the exposures are very short, while in the extreme ultra violet they are very long. Under the same conditions of plate and slit opening, a casette setting at 3700 Å. U. may require an exposure of six seconds; but with a casette setting at 2500 Å. U., the required exposure may be 30 minutes. It is difficult to obtain satisfactory photographs below 2200 Å. U. unless special plates are used. The air itself rapidly absorbs light of small wave lengths. In ordinary analytical work there is no reason for observations below 2500 Å. U., because most elements give a number of lines in the region between this point and the visible spectrum. Correct exposure times are easily determined by a series of test exposures.

It is probable that most spectrum photographs are made on plates rather than on films. The use of plates has a number of disadvantages which are particularly noticeable when the methods of reading, which will be described, are applied. In the writer's work, films have always been used. They are easily stored for reference, are not subject to breakage, and may be readily cut to size for enlargement reading. No trouble whatever has been met in the matter of stretch or distortion.

Some study has been made as to the best type of emulsion for the purpose. For work in the ultra violet region, either Eastman "Commercial" or "Commercial Ortho" cut films have been found to be suitable and satisfactory. The Commercial film has less tendency to fog, but is quite insensitive in the yellow and red of the visible region. Commercial Ortho film is yellow sensitive and somewhat faster than Commercial in the ultra violet, but has some tendency to fog. For general visible spectrum work, where photographs of the red region are required, some form of panchromatic film will be necessary. Process panchromatic emulsions have been found to be very satisfactory. Work in the infra red region requires

specially dyed plates, but work in this region is outside the scope of this article and these plates therefore need not be considered. The casette used takes a plate or film 4 x 10 inches. The films are purchased 8 x 10 inch size and cut in half. About 16 exposures can be made on one 4 x 10 inch film.

Some authorities recommend the use of certain "contrasty" developers for spectrum work. Comparative tests have been made with a large number of developer formulae, but it has been found that if the negative is given full development, the type of developer has little or no bearing on the results obtained, except in the case of panchromatic emulsions. For general work Eastman's Elon D-11 formula has given satisfaction. This is a fast developer requiring 5 minutes at 65 degrees Fahr. Where the negatives are to be subjected to great enlargement, it is believed that real advantage in the production of small grain size may be obtained by the use of Eastman's Borax developer formula D-76.

Methods of Reading Spectrograms

Several methods may be used for reading the spectrograms for the identification of lines and determination of their wave length. A comparatively simple method which does not involve the use of an expensive micro comparator is to prepare a set of spectrum negatives using pure salts of the various elements in an arc of purified carbons. It is not a difficult matter to identify and mark in the wave lengths of the principal lines on the negatives, and then compare the unknown spectrum with the set of negatives. This method becomes rather complicated and somewhat uncertain when complex substances are under investigation, but may be sufficient in some cases. It is a great aid if an iron spectrum photograph is imposed beneath the unknown spectrum so that it may be used for purposes of orientation. Certain of the prominent iron lines may be recognized by comparison with the enlargement of the iron spectrum published by Adam Hilger, Ltd., London.

The most usual method of identification is by means of the micro comparator. This instrument consists of a microscope mounted on an accurate lead screw so that it may be traversed along the spectrum negative which is illuminated by transmitted light. The lead screw is fitted with an indexed head in order that the distance between lines may be exactly measured. In this case a pure iron

spectrum is used as a guide. The wave length of lines having been determined, their identity must be established by reference to a list of spectra such as appears in the International Critical Tables. When spectrographs from prism instruments are read in this way, the calculation of exact wave lengths is greatly complicated by the non-uniformity of the dispersion. Another method is one suggested by Adam Hilger, Ltd., by the use of "R. U. powder."[5] This powder has been developed by J. W. Ryde and H. C. Jenkins at the Research Laboratories of the General Electric Company, Ltd., Wembley. This powder consists of small quantities of fifty elements incorporated in a base material composed of zinc, magnesium, and calcium oxides. The quantity of each element present has been carefully adjusted so that only the "raies ultimes" (most persistent lines) and the most important sensitive lines appear when the spectrum is excited by placing some of the powder in the ordinary electric arc. On the average, about seven lines appear per element. All the elements present are evenly distributed throughout the bulk of the powder so that, under controlled conditions of excitation, the same composite spectrum is produced. When used as a comparison spectrum, the sensitive lines of all the elements present as impurities in the substance under examination will coincide with the corresponding lines in the "R. U." spectrum. A tabulation, as well as a set of enlargements of the arc spectrum (from a prism instrument) has been prepared. The origin of each line is marked so that all the elements present in the sample may be readily identified.

The tediousness of the usual methods of line identification, especially when applied to iron alloy spectra, lead the writer to adopt other means such that the great complexity of the iron spectrum was turned into an aid rather than a hindrance. It is believed that the methods to be described are easier of application and may be operated with greater speed, having due consideration for accuracy, than any which have come to the writer's attention. It is true that considerable preliminary work is necessary, but when once this is accomplished it is done for all time. Reference is made to the production of visual charts or spectrum atlases.

The original spectrograms produced with the 21-foot grating have a dispersion such that one inch contains about 66.5 Ångstrom units, or 1 Å. U. = 0.015 inch. This represents an initial magnifi-

[5]Adam Hilger, Ltd., London, 4th Ed., "The Practice of Spectrum Analysis," 1929, p. 24-25.

cation of about 3,800,000 times. Even with such a high dispersion, the differentiation of the lines of the iron spectrum is difficult with the unaided eye. The upper portion of Fig. 9 shows a portion of the spectrum of chromium-vanadium steel at the original scale. A method of reading was adopted in which an enlargement of $8\frac{3}{10}$ times is made of the original negative, giving a spectrogram such

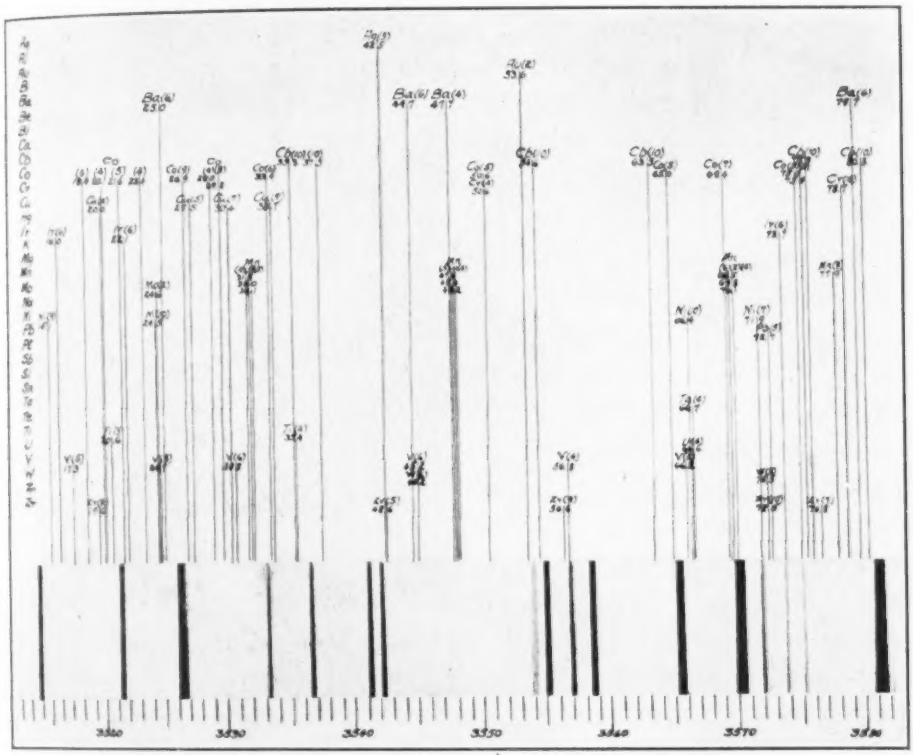


Fig. 8—Plate from Spectrum Atlas. Reduced to 2/5 Original Size.

as is shown at the bottom of Fig. 9. In these cases the magnification is equivalent to 32,000,000 times, so that one inch equals 7.8 Å. U. or 1 Å. U. = 0.127 inch = 3.2 millimeters.

In the preparation of the first chart, an enlarged iron spectrum photograph was made from 2400 to 4000 Å. U. in strips about 10 inches long, which were attached to sections of heavy white cardboard measuring 8 x 10 inches. Under each section was drawn a numbered scale in units of one Ångstrom. Above each spectrum strip was drawn the position of every spectrum line, as shown in the International Critical Tables, for about thirty elements commonly met with in metallurgical work. The total number of chart cards

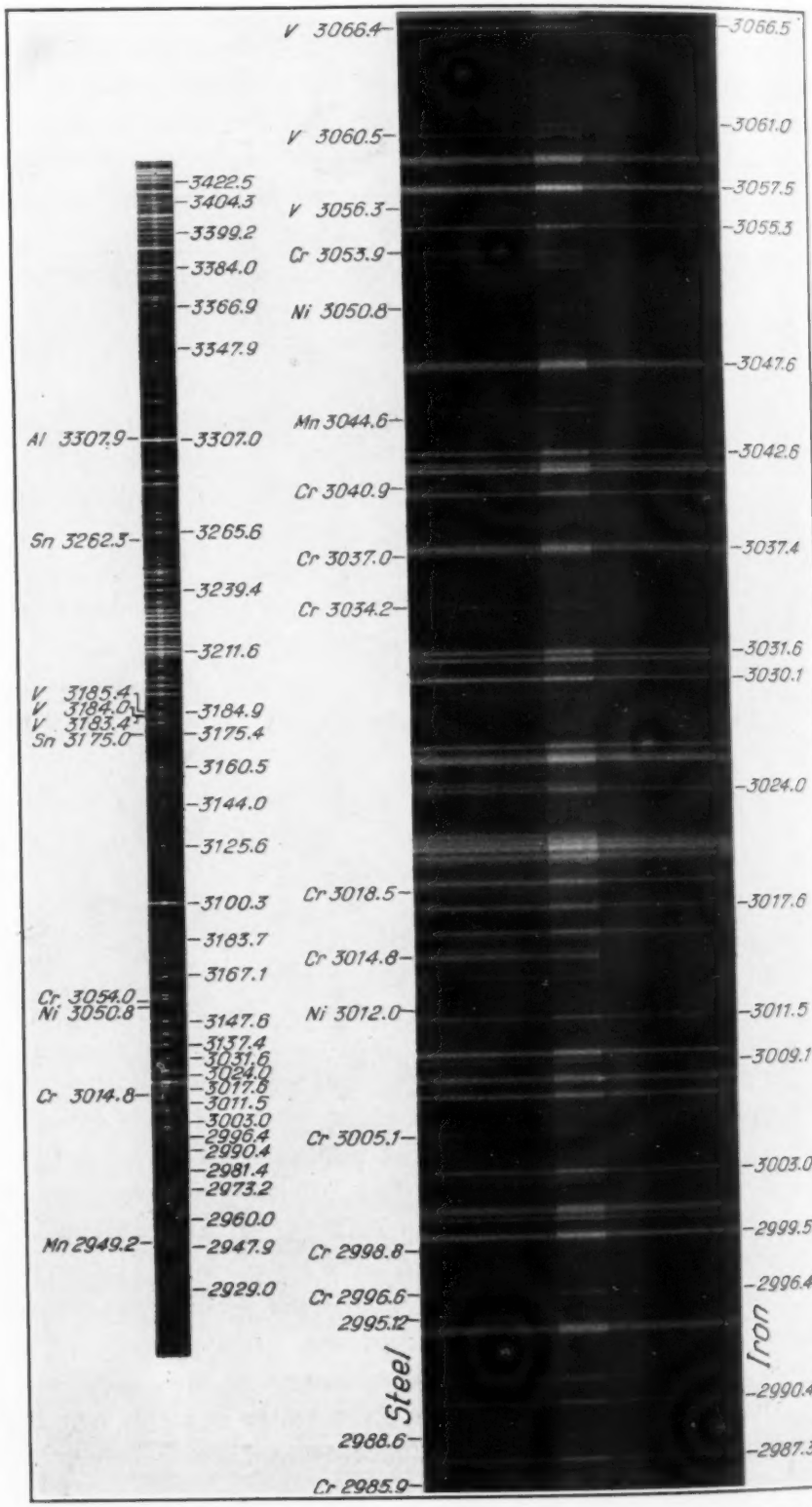


Fig. 9—Portion of Spectrum of Chromium-Vanadium Steel. Reduced to 2/3 Original Size.

in the set is 24, making a total spectrum length of 20 feet. The appearance of one of the cards is shown at a reduced scale in Fig. 8.

The method of application is as follows. Before the exposure for the spectrogram of the unknown material is made, an iron spectrogram is exposed on the film. The ratchet on the casette is turned up one notch and the unknown spectrum exposed. Care is taken to allow no lateral displacement of the casette. When the film is developed the iron spectrum should lie below the unknown spectrum. When the film is dry it is placed in a photo enlarger. The enlarger is adjusted so that the iron guide spectrum on the film exactly matches the iron spectrum lines on the chart. The projection shadow of the unknown spectrum will then lie on the chart above the shadow of the matched iron spectrum shadow. Any lines occurring in the unknown spectrum and not occurring in the pure iron guide spectrum immediately become apparent, and their identity is at once established by their coincidence with the ruled position lines of the various elements. A reading of a spectrum strip covering 600 Å. U. may be made in less than five minutes. This chart has been found to be of the greatest use and convenience, but it contains a record of only about thirty elements and shows only those lines given for these elements in the International Critical Tables.

It will be noticed that the iron reference spectrum on the chart is reversed; that is, the lines are black instead of white. This was purposely arranged because the projected lines from the negative under study also appear black. It is found that it is easier to match black to black rather than black to white. The iron spectrum on the chart also appears to be poorly reproduced; only a few of the many lines really present are shown. This is also intentional because it has been found difficult to "find oneself" by matching two complete iron spectra, on account of the great multiplicity of lines and the complication of the line pattern.

Spectrum Ghosts

Unless one is fortunate enough to have available one of the few "perfect" gratings, some trouble may be experienced with "ghosts." In regard to ghosts, Baly[6] states:

"Bell points out in his paper that the grating space is never regular throughout the whole extent of the ruled surface and the

[6] E. C. C. Baly, "Spectrometry," Vol. I, pp. 33 and 159.

variations may be classed as regular and irregular. In the first class are put those which are periodic or linear, which produce respectively 'ghosts'—that is to say, false images and differences in focus on opposite sides of the normal.

"As regards the effect produced by errors in ruling, those arising from periodic errors may be mentioned. By periodic errors is meant the continual repeating of some false ruling; this usually arises from some defect in the ruling machine which occurs at every revolution of the screw. The effect of errors of this kind is to produce false images of lines, which are called 'ghosts.' With a good grating these lines are often nonexistent but they may, in cases, assert themselves so much as to render a grating useless. It is the bright lines which most readily, of course, give rise to ghosts, and the latter may be recognized by their appearing as weak lines symmetrically placed on each side of the brighter lines. Roland has investigated the general theory of the effect of errors in the ruling of gratings; as regards the ghosts arising from the periodic errors he found that the intensity of ghosts of the first order is proportional to the square of the order of the spectrum considered and to the square of the relative variation from the true grating interval."

When an iron standard is used as a reference it is essential in careful work to locate the ghosts present. Otherwise, ghosts may be taken either as iron lines or as lines of impurities in the iron. The presence of unidentified ghosts also tends to the finding of mysterious "unknown" lines.

Ghost lines are not only symmetrical—that is, they lie exactly at the same distance on each side of the lines of origin—but their distance on each side of the origin line is exactly proportional to the wave length. In other words, if at 3000 Å. U. the distance of the ghost each side of the origin line is 3.0 Å. U., then at 4000 Å. U. the ghost interval will be

$$\frac{3.0 \times 4000}{3000} = 4.0 \text{ Å. U.}$$

With these conditions in mind, a line suspected of being a ghost may be tested by measuring off the proper calculated distance on each side, depending on the wave length, and finding if a bright line is present. In such a test the scale of enlargement or the exact dispersion scale must be known. The fact that a ghost always has a partner at an equal distance on the other side of the origin line is

made use of. In order to determine the ghost intervals so that they may be located and marked on another atlas, which will be described later, a spectrogram of the mercury arc was made. The element mercury was chosen because it gives bright lines which are few in number, especially in the ultra violet region. The spectrograph negative was enlarged to the chart scale and the ghost intervals of several sets of ghosts measured with the following results:

Wave Length	Width of Ghost from Origin Inches
3022	0.515
3125	0.535
3650	0.600
4047	0.660
4078	0.690
4339	0.725

From these data the ghost intervals can readily be calculated for any desired portion of the spectrum.

The second chart or atlas prepared consists in an iron spectrum (of Armco iron) in which every iron line recorded by Burns in Watts' Index of Spectra,[7] from 3000 to 4200 Å. U., was identified and the corresponding wave lengths recorded. In addition, the lines of all the impurities in the Armco iron were located, as well as the position of all visible ghosts. Each section of the chart was mounted on 8 x 10 inch heavy cardboard. Ten cards constitute the set. The working chart has a dispersion such that one inch equals 8.017 Å. U., or 1 Å. U. is equivalent to about 1/8 inch.

In ordinary metallurgical analysis, the first chart described has been found adequate for all ordinary determinations. Generally the presence of ghosts or other unidentified lines is immaterial. In some cases, for instance, in the analysis of minerals which may contain some of the rarer elements or where exact determinations are imperative, or when all lines must be accounted for, the use of the second chart is of great convenience and is almost essential.

The method used in constructing the second chart may be of interest. A continuous over-lapping set of enlargements of a carefully photographed Armco iron spectrum was prepared, covering the region of the spectrum desired. Starting with the first strip and referring to Watts' Index of Spectra, several prominent iron lines occurring in the strip were identified and the exact dispersion of the

[7] W. Marshall Watts, "Index of Spectra," Appendix Z, 1931, p. 52.

strip determined. A tabulation for the strip was then prepared, using several prominent lines as a basis. All the recorded lines in the Index were recorded and their difference in Å. U. from the base lines first chosen, written in. From the dispersion previously calculated, the distances in Å. U. were converted to inches and recorded. With a pair of dividers, a reading magnifier, and an accurate steel scale divided into 1/100 inch, the position of every line in the spectrum strip was located and checked. The wave lengths were then written in. Lines still unaccounted for must fall into four categories: first, impurity lines; second, ghosts; third, lines of iron not recorded in the index; fourth, unknown lines. The wave length of each of these lines was located and marked. In this way over 1500 lines were recorded on the chart.

The chart thus constructed may be utilized in several ways. A spectrogram of an unknown sample may be prepared by means of the Pfund arc or the carbon arc. In the first case an iron reference spectrum will not be absolutely necessary, but with the carbon arc an iron reference spectrum should be included. In either case enlargements of the spectrum negative are made to the chart scale and compared with the chart. The wave lengths of lines other than iron in the "unknown" spectrum may easily be estimated by eye with sufficient accuracy for identification in the International Critical Tables. For great accuracy of wave length determination, the unknown lines may be scaled off with a dividers and calculated. The projection method described above can also be applied if desired.

Results Obtained

This article will be concluded by discussing a few examples of the results that have been obtained by the methods which have been described. Most of the writer's work has been in connection with the spectrum analysis of steel and ferrous alloys. This particular class of work presents many difficulties to the worker using the smaller types of prism instruments ordinarily found in chemical laboratories, but is easily accomplished with the 21-foot grating apparatus.

In Fig. 9 is shown a spectrum of a chromium-vanadium steel. In the upper spectrograph the elements chromium, silicon, tin, copper, manganese, tungsten, vanadium, and nickel may readily be identified by the reading methods which have been described. The lower

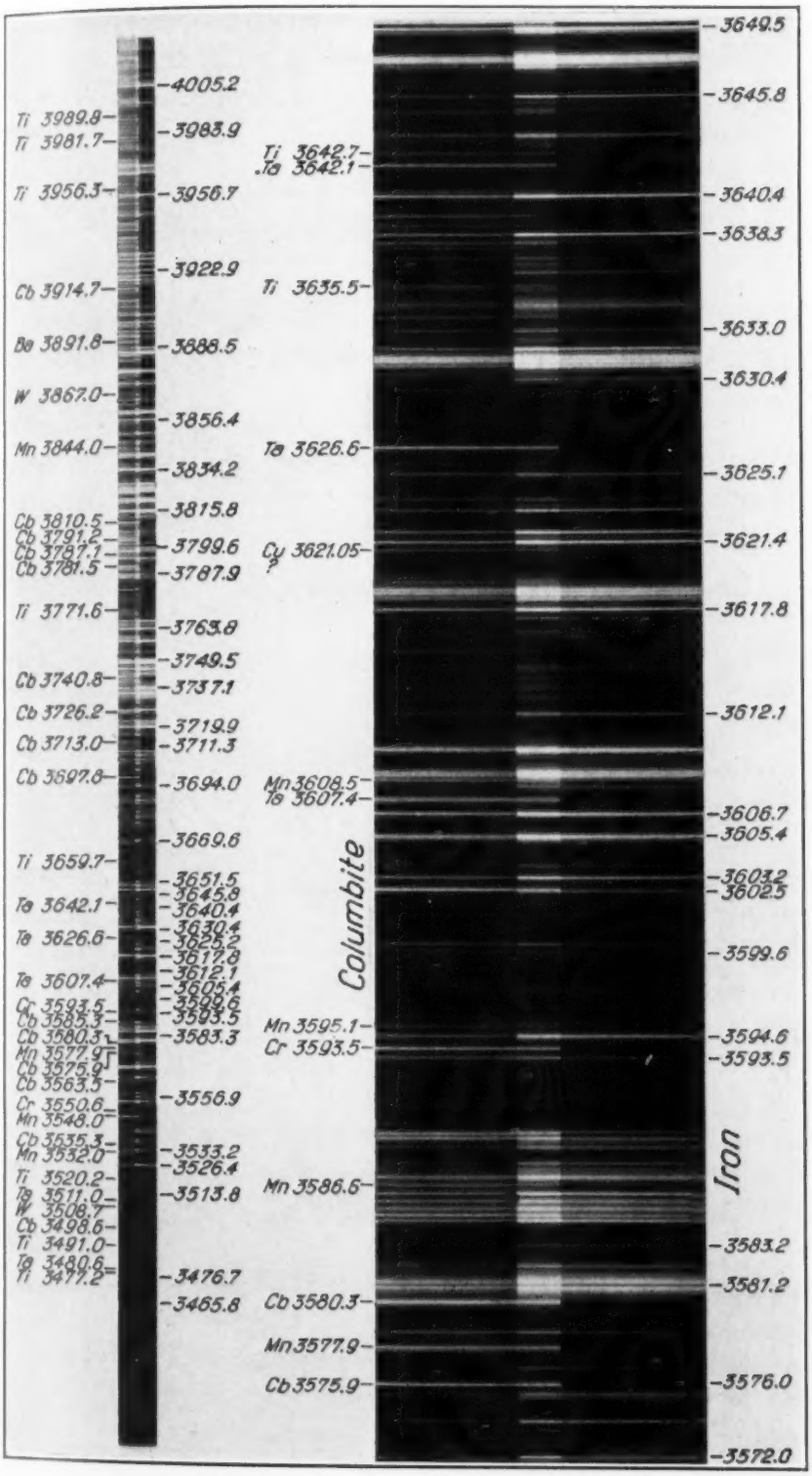


Fig. 10—Spectrum of Columbite. Reduced to 2/3 Original Size.

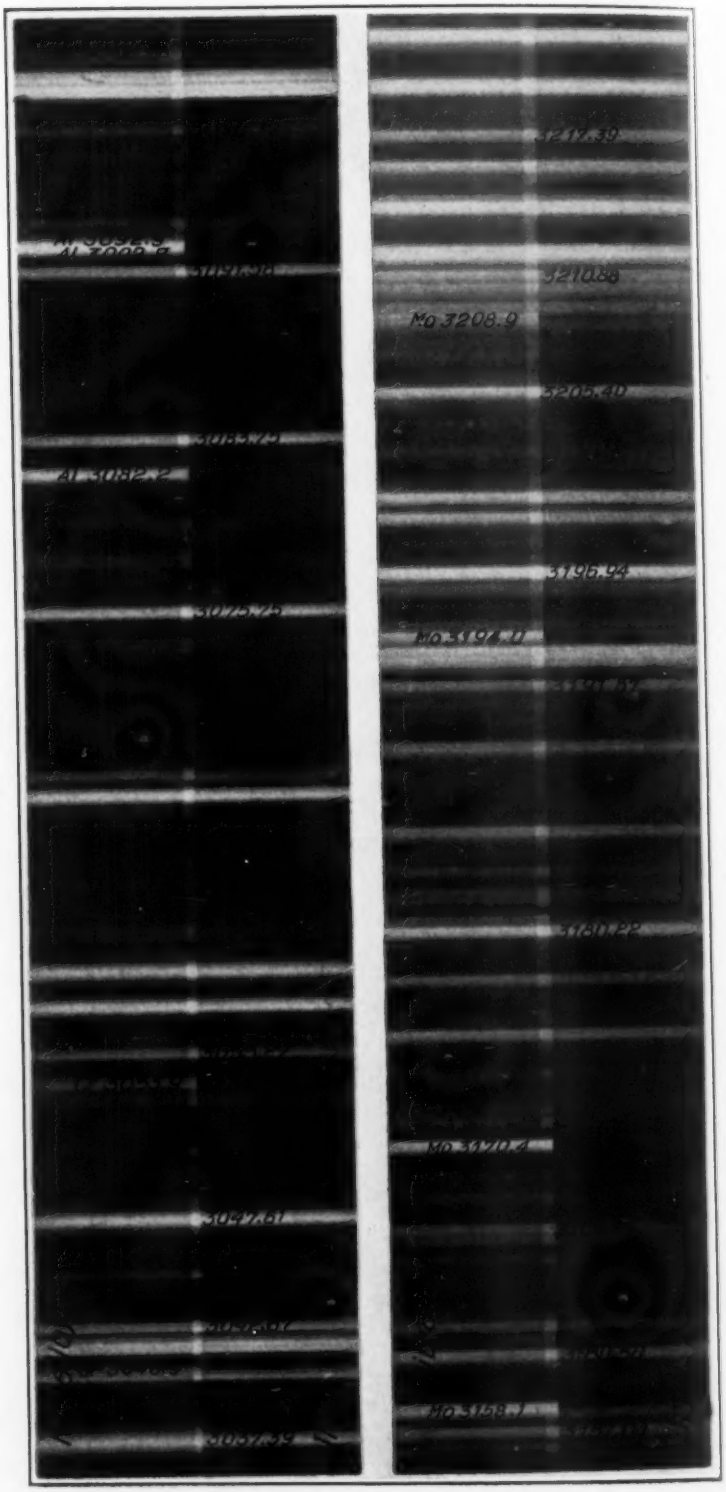


Fig. 11—Spectrum of Nitralloy Steel.

enlarged section of the spectrogram shows the region, between 2987 and 3066 Å. U., enlarged to the reading scale and in which a few lines have been marked.

The identification of metallic elements in some of the rarer minerals, which are becoming of increasing importance in later years, often offers considerable difficulty in the chemical laboratory. The spectrum analysis of a sample of the mineral columbite from South Dakota may be used as an illustration. This mineral, essentially a columbate of iron, contains a number of other metallic elements, some of which are difficult to separate and identify by chemical methods. Fig. 10 shows a spectrogram of this mineral between about 3460 and 4005 Å. U. In the illustration a number of the prominent lines in the iron guide spectrum have been identified and their wave lengths recorded. It is quite feasible to identify these iron lines by comparison with some published iron spectrum, for instance that of Adam Hilger, Ltd. The identity of prominent lines in the mineral spectrum can then be located and identified by measurement. In the case under discussion, the dispersion in the original photograph is such that one Å. U. equals 0.015 inch or one inch equals 66.5 Å. U. With a pair of dividers and a 1/100 inch steel scale, all the prominent lines may be measured with sufficient accuracy for identification by means of the data in the International Critical Tables. A more convenient reference is one in which all the lines are arranged in numerical sequence rather than by element groups. Watts' Index of Spectra, Appendix U, 1911, is arranged in this manner.

The method described is tedious and time consuming. Many of the fainter lines will be missed, as well as those which reside close to lines of iron. For careful work and where the more easily applied projection method of reading is used, the negative is enlarged to the scale shown in the lower portion of Fig. 10. In this figure a few of the lines have been identified and marked. If the spectrum negative is placed in a projector and the projected image used in connection with the first spectrum chart described in this article, the six hundred Å. U. strip shown in Fig. 10 can be run over in a few minutes. Using this method on a spectrum negative, a total of 41 lines were located and recorded in less than ten minutes. By using the projection method of reading, in which the dispersion is increased to a point where 1 Ångstrom unit measures approximately ⅛ inch, lines that are very faint or that are closely adjacent to iron lines may readily be identified with a minimum consumption of time.

Since this article was written, a complete new set of charts has been prepared, at a scale — 1 Å. U. = 5 millimeters, covering 33 common elements and recording all the lines available in the literature. The charts include 700 Å. U. in the ultra violet and a like area in the visible spectrum. A total of about 14,000 lines is recorded. These charts, as well as a consecutive index of all lines of all the metallic elements occurring in the areas covered by the charts, are now in course of publication.

ON THE INFLUENCE OF HYDROGEN ON THE TRANSFORMATIONS IN IRON

By Hans Esser and Heinz Cornelius

Abstract

The modified method of thermal analysis described in this paper brings out the fact that the doubling of the A_3 transformation is due to the absorption of hydrogen during annealing rather than to impurities in the metals used in some previous researches.

The greater degree of accuracy in the present method is made possible by the small size of the specimens used and the briefness of the application of electric current in welding.

Proof of the absorption theory is shown by the fact that the doubling is removed by degassing.

IN their work concerning the critical ranges in the system iron-carbon, Harrington and Wood[1] have presented metallographical and thermal investigations of 32 pure steels. The most important result of this work is the proof that the A_3 and A_1 transformations take place in two stages which can be recognized as separate effects on the differential thermal analysis curves. Such double effects have not been observed by earlier workers. This led Harrington and Wood to the suggestion that less pure samples had been used in previous researches.

Some of the thermal differential curves of Harrington and Wood for steels of various carbon contents are shown in Figs. 1 and 2. The double effects at A_1 and A_3 transformations can be very plainly seen. The portion of the iron-carbon system, taken from the heating curves, is shown in Fig. 3. The diagram shows two bent lines which represent the temperature of the A_3 transformation plotted against carbon content. The two effects which were found for the A_1 transformation have however been represented by only one line. A number of details in which Fig. 3 differs

[1]R. H. Harrington and W. P. Wood, "Critical Ranges in Pure Iron-Carbon Alloys," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 632.

Dr. Hans Esser, special lecturer, materials testing and metal treatment, Institut für Eisenhüttenkunde, Aachen, Germany. Manuscript received March 15, 1933.

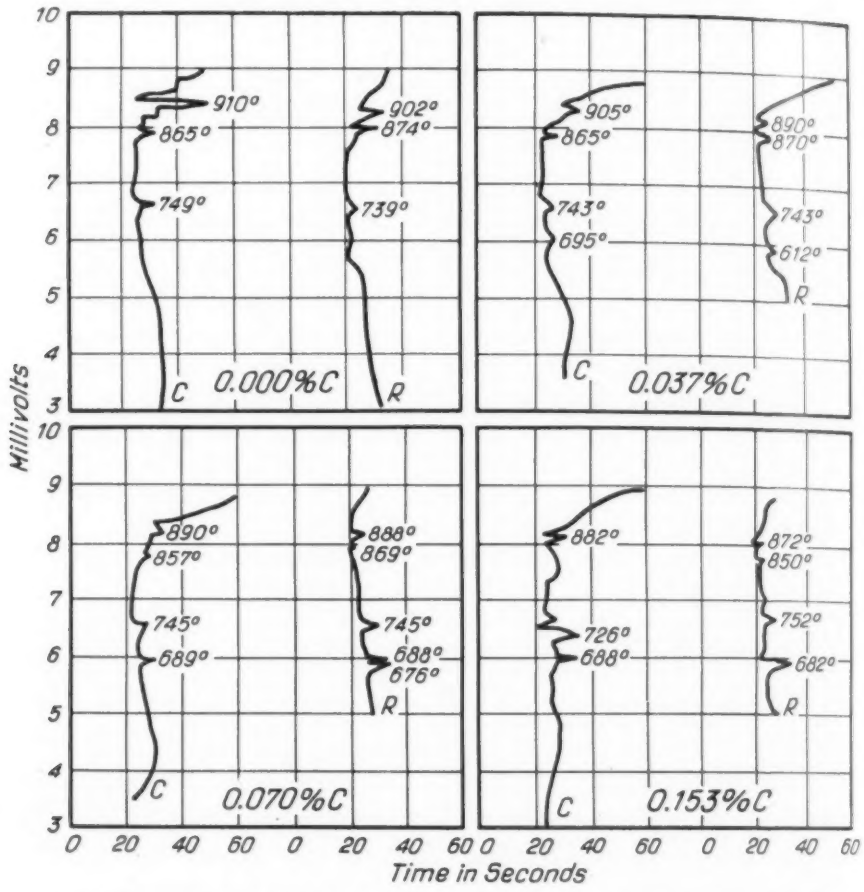


Fig. 1—Heating and Cooling Curves of Steels with Carbon Contents as Indicated (Harrington and Wood).

from the customary interpretation of the iron-carbon system, are here of secondary importance and will not be further discussed.

In a more recent work, Harrington and Wood[2] have confirmed the two-step transformations at A_1 and A_3, and thereby suggest a theory for the nature and the mechanism of the allotropic transformations of iron and iron-carbon alloys.

The connection between the work of Harrington and Wood and the present paper on the influence of hydrogen on the A_1 and A_3 transformations is due to the method of preparation of the former's samples. This method is based on the fact that at 960 degrees Cent. (1760 degrees Fahr.) in a constant atmosphere of dry hydrogen, equilibrium between all the iron and all the carbon is reached in six days. For instance, with a specimen of 0.6 per cent carbon steel

[2]R. H. Harrington and W. P. Wood, "Allotropy in Iron and Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 20, 1932, p. 529.

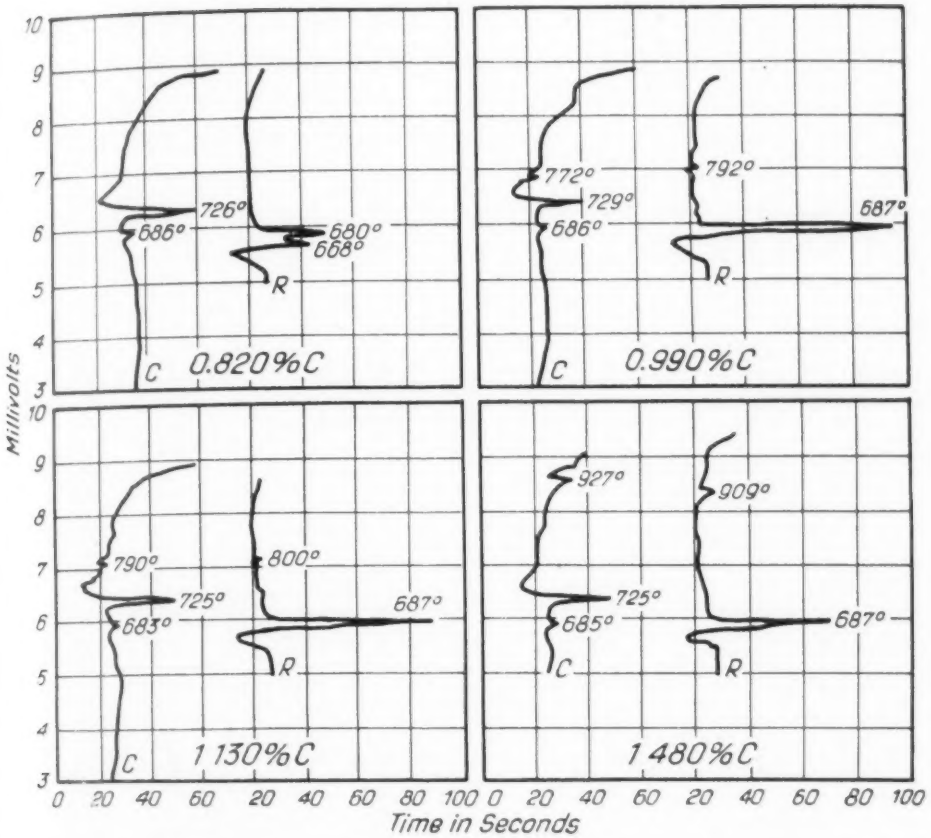


Fig. 2—Heating and Cooling Curves of Steels with Carbon Contents as Indicated (Harrington and Wood).

and two other specimens of pure iron (all the same size) one obtains three specimens each of 0.2 per cent carbon content. In this method of preparation the iron cannot be prevented from absorbing a large quantity of hydrogen.

The present investigation was carried out with the help of a modified method of thermal differential analysis which gave a greater degree of accuracy than previous methods. The specimens consisted of small plates with 0.5 millimeter thickness and 4 millimeter diameter. A specimen of chronin (90.0 per cent nickel, 10.0 per cent chromium) was used as the standard sample. The thermocouple wires were attached to the specimens by electrical contact welding. The welding apparatus consisted of a small vise in which the specimen was gripped, and so formed one terminal of the electrical welding circuit. The other terminal consisted of a copper point which was pressed on to the specimen by a spring. For welding, one end of the thermocouple wire was pressed on to the specimen by

the copper point. The welding current (3-6 volt, 100 ampere) was then switched on for about one-tenth of a second by a button switch. Owing to the short time necessary for the welding and also owing to the cooling of the specimen by the vise, oxidation only took place in the neighborhood of the small welded spots.

The small specimens used by the present writers make it possible to realize the same temperature throughout the whole speci-

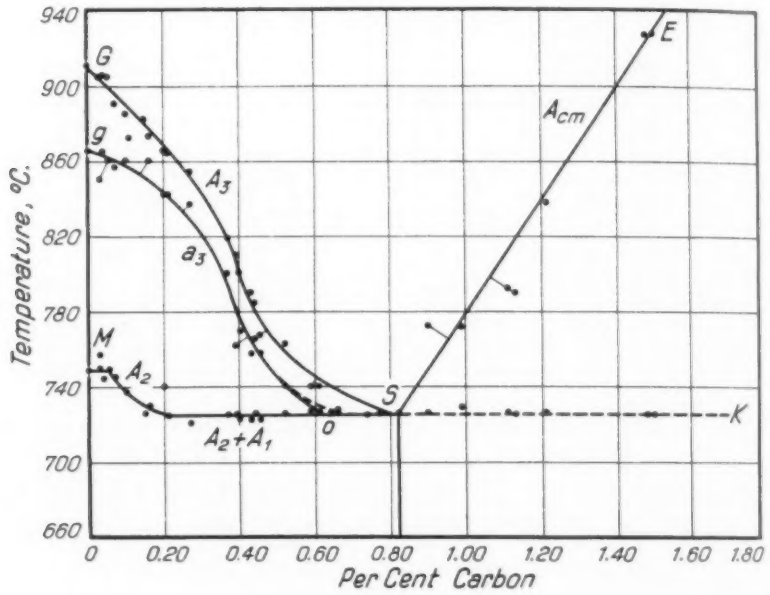


Fig. 3—Diagram Obtained by Plotting Points Observed on Heating the Specimens (Harrington and Wood).

men, and to keep the specimen and the standard in a region of equal temperature. Since the specimens form the welds of the thermocouples, any thermal effects are registered without any lag. In the investigation of the influence of gases, small plates are very suitable, since they offer rapid diffusion of the gas into the middle of the specimen. Fig. 4 shows the arrangement of the specimens in the furnace.

Before the treatment with hydrogen a thermal analysis curve was made of the sample in its original condition. Then the specimen was annealed in hydrogen under a pressure of a half to one atmosphere and thermal curves on cooling and heating in an atmosphere of hydrogen were registered. The hydrogen was prepared electrolytically, purified and dried.

Fig. 5 shows the thermal differential curves of electrolytic iron

(a) in its original condition and (b) after one hour of annealing in hydrogen at 1200 degrees Cent. (2190 degrees Fahr.). The influence of this thermal treatment in hydrogen is shown by a definite doubling of the Ac_3 and Ar_3 points.

In a further experiment, a steel of 0.75 per cent carbon; 0.12 per cent manganese; 0.10 per cent silicon; 0.021 per cent sulphur; 0.01 per cent phosphorus was investigated. The differential curve

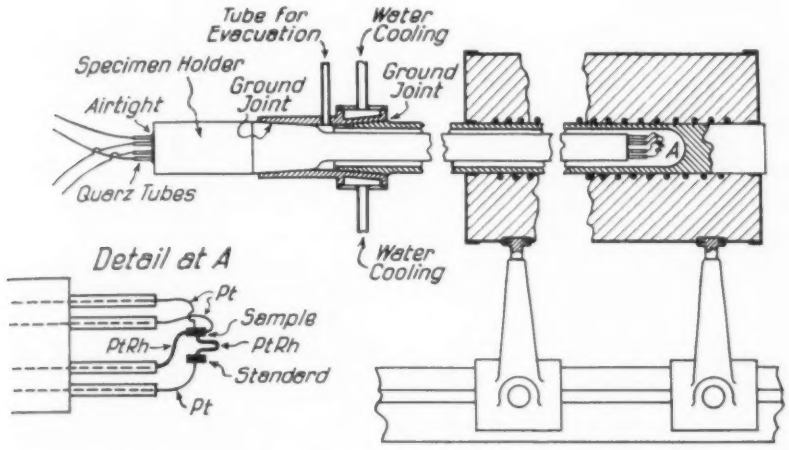


Fig. 4—Arrangement of Samples and Furnace for Thermal Differential Analyses.

of this steel is shown in Fig. 6. The same specimen was decarburized by annealing in hydrogen at 850-950 degrees Cent. (1560-1740 degrees Fahr.), then heated to 1000 degrees Cent. (1830 degrees Fahr.), and cooling and reheating curves were taken. The doubling of the A_3 effect is already noticeable (Fig. 7 No. 1). The following graphs on the Saladin apparatus show a clearer appearance of the doubling at Ar_3 (Fig. 7, No. 2). This is very definite after three minutes annealing in hydrogen at 1200 degrees Cent. (2190 degrees Fahr.) (Fig. 7 No. 3). After cooling in hydrogen the same specimen was left for one day in contact with air and then again investigated

Table I

Temperature of Transformation Points After Annealing in Hydrogen. Degrees Cent.

Curve No.	Original Material	Ac_2 Maxima	Ar_2 Maxima	Ac_3 1. Maxima	Ac_3 2.	Ar_3 1. Maxima	Ar_3 2.
1	0.75 Per Cent Carbon Steel	772	770	921	932	...	910
2	0.75 Per Cent Carbon Steel	769	768	920	932	908	910
3	0.75 Per Cent Carbon Steel	775	772	924	938	908	910
4	0.75 Per Cent Carbon Steel	775	773	923	936	908	910
5	0.75 Per Cent Carbon Steel	764	769	...	928	...	912

(Fig. 7 No. 4). The doubling took place with equal intensity. It however disappeared completely after heating the specimen in a high vacuum to 1300-1400 degrees Cent. (2370-2550 degrees Fahr.) and afterwards cooling in a high vacuum down to room temperature. The curve taken after this treatment (Fig. 7 No. 5) shows only one (small) effect for the A_3 transformation. This series of experi-

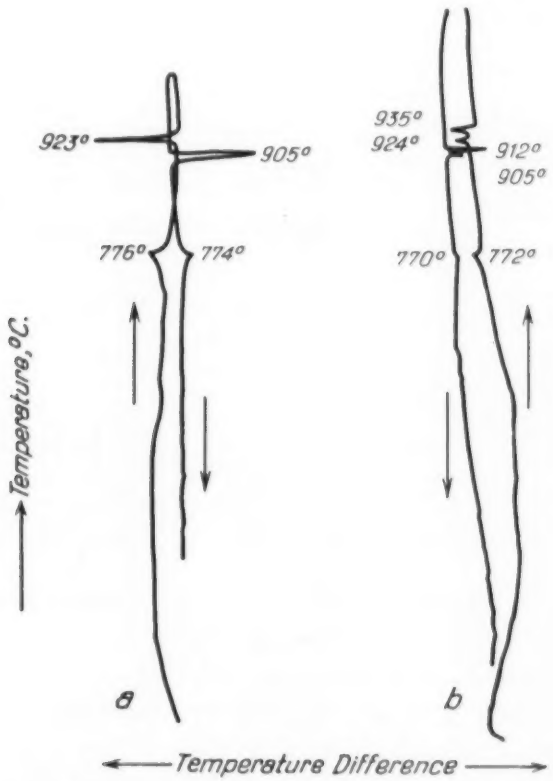


Fig. 5—Influence of Hydrogen on the A_3 Transformation. Electrolytic Iron.

ments with the 0.75 per cent carbon steel makes it clear that the doubling of the A_3 transformation after annealing in hydrogen is due to the absorption of this gas. This is confirmed by the frequently repeated observation that the doubling of the thermal transformation effects is removed by degassing. The temperatures of the maxima at A_3 for the curves in Fig. 6 are shown in Table I.

Starting with various kinds of pure iron (electrolytic iron, iron prepared by the carbonyl process) and carbon steel, the experiments on the influence of hydrogen on the A_3 transformation of practically carbon-free iron were repeated and confirmed. This influence could also be confirmed by dilatometric analysis.

A doubling of the A_1 transformation effect was established also on a steel with 0.57 per cent carbon, after annealing for a few minutes in hydrogen above Ac_1 (Fig. 8).

In view of these experiments one can safely say that the double

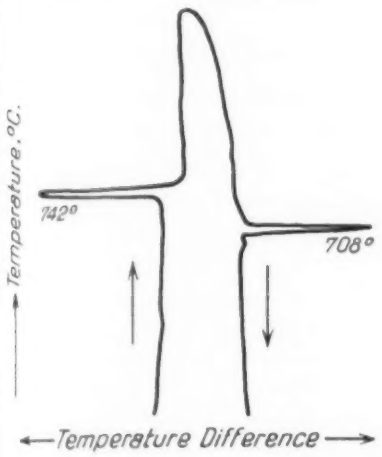


Fig. 6—Heating and Cooling Curves of 0.75 Per Cent Carbon Steel.

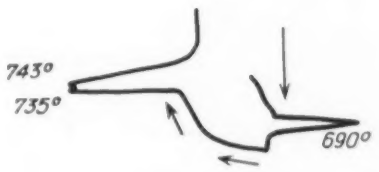


Fig. 8—Influence of Hydrogen on Ac_1 Transformation of 0.57 Per Cent Carbon Steel.

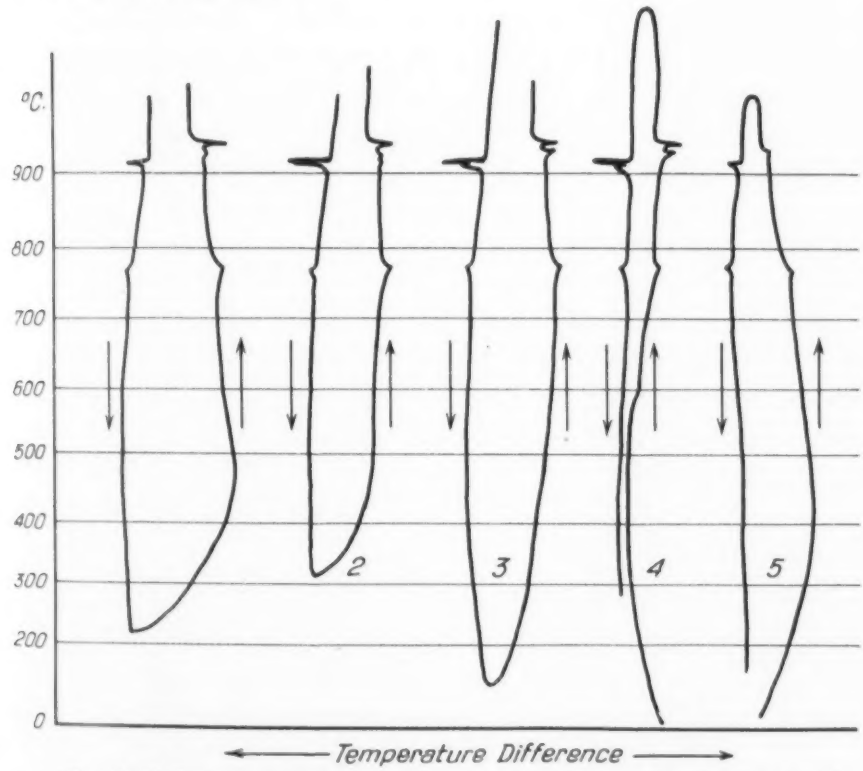


Fig. 7—Influence of Hydrogen on A_3 Transformation. Original Material 0.75 Per Cent Carbon Steel.

effect for A_1 and A_3 transformations, observed by Harrington and Wood, is due to their method of preparation of the samples, in which hydrogen must have been absorbed. The discussion of two-step transformations at a property of pure iron and pure iron-carbon alloys is therefore apparently unnecessary.

A theoretical explanation of the influence of hydrogen on the transformations in the system iron-carbon cannot yet be given.

The fact that through absorption of hydrogen in iron a second A_3 point can appear, shows that the allotropy of iron depends greatly on the degree of purity of the iron. Chemically and physically pure iron, as indeed Yensen already considers, will perhaps be found to possess no polymorphic modifications.

Summary

Harrington and Wood have found two-step transformations in the iron-carbon system at A_1 and A_3. Their samples, prepared by annealing in hydrogen, must have absorbed this gas. In the present work, carried out with a modified method of thermal analysis, this doubling effect was found only in specimens annealed in hydrogen. After degassing, only a single thermal effect was observed. It is suggested that the double effect, found by Harrington and Wood, was due to hydrogen contained in their specimens.

MECHANICAL HARDNESS, INFLUENCED BY MAGNETISM AND MEASURED BY MAGNETOSTRICTIVE EFFECTS

By S. R. Williams

Abstract

This paper deals with the problem of mechanical hardness and the methods employed in measuring it. At present there is no uniformity in the measurements of hardness. Hardness is one thing for one manufacturing plant and something else for another.

In studying the changes in length of ferromagnetic rods, when magnetized longitudinally, it was found that variations in mechanical hardness varied this magnetostrictive effect in a very interesting way. In fact, this longitudinal change of length in a magnetic field was found to have possibilities in it as a means for measuring hardness. An extensive study has been made of this relation between magnetostriction and mechanical hardness. During the study it was discovered that a magnetization process itself produces changes in hardness. The first effect is to reduce the hardness.

TOWARD the close of the World War the engineering division of the National Research Council formed a committee whose purpose should be the investigation of the methods in use for measuring mechanical hardness. Among other duties, the committee was asked to report on the possibility of formulating a general definition for mechanical hardness. As a member of this committee it will perhaps be made clear how a physicist became enmeshed in what at the time seemed more or less of a metallurgical problem. Fundamentally it is a physical problem for which no apologies need be offered for an interest in it.

Definitions of Hardness

In general, physicists have not recognized hardness as one of the essential properties of matter, while the engineers have considered it to be of fundamental importance. There seem to be two

The author S. R. Williams is a member of the society and is professor in the department of physics, Amherst College, Amherst, Massachusetts. Manuscript received December 19, 1932.

general classes of hardness: 1. surface or superficial skin hardness which is referred to as resistance to abrasion, 2. penetration, often spoken of as deformation hardness. Both are closely associated and in practice one seldom occurs without the other.

As a working definition, the committee adopted the following: "Hardness is the cohesive resistance of a molecular aggregate structure of a material to any deformation of form." This is an academic statement which will, in all probability, not satisfy anyone. Tiemann[1] defines hardness as—"The resistance offered by a body to abrasion or penetration." This covers the two types of hardness referred to above. Jeffries and Archer[2] define this property—"Hardness is resistance to permanent deformations." "Hardness may mean resistance to indentation, as measured by the Brinell test, resilience, as measured by the Shore scleroscope, scratch hardness, cutting hardness, resistance to machining, or some other special kind of hardness." These definitions indicate that mechanical hardness is closely associated with the elastic properties of matter. The elastic properties in turn, as will be indicated later, are intimately linked with the magnetostrictive effects.

Methods of Measuring Hardness

As one goes over the various methods employed in measuring the property of hardness, one is impressed with the fact that we do not all mean exactly the same thing when we use the term hardness. The scratch method was one of the early methods employed for designating the relative hardnesses of materials. Moh classified a set of materials which would scratch the previous substance in the list. The hardest one in the list being diamond.

Moh's List

1 Talc
2 Crystallized Gypsum (Rock Salt)
3 Calcspar (Calcite)
4 Fluorspar
5 Apatite
6 Felspar
7 Quartz
8 Topaz
9 Sapphire (Corundum)
10 Diamond

[1]Hugh P. Tiemann, Iron and Steel, 1919, McGraw-Hill Book Company, New York City, p. 198.

[2]Zay Jeffries and R. S. Archer, "The Science of Metals," 1924, McGraw-Hill Book Company, New York City, p. 403.

This scale of hardness comes more nearly than any other in representing to the lay mind the general meaning of the term.

Taking up hardness tests as now employed, the leading methods are the static indentation methods. This consists of forcing into the material a hardened steel ball, or special diamond point, under a standard load. Either from the size or the depth of the indentation, a measure of the hardness number is obtained. In the Moh scale the numbers, 1 to 10 are only relative. They have no absolute value.

The dynamic indentation, or driving-in-method, is measured by a scleroscope. This consists of a small diamond pointed hammer falling freely in a graduated glass tube from a constant height. The height of rebound is said to measure the hardness of the surface from which the hammer bounced. Then there are impact tests, tests of resistance to wear, endurance tests, ductility tests and many others, each one of which measures some specific property that is intimately related to hardness and so we call it measuring the hardness of the material.

Forces Involved in Hardness

In each type of hardness testing, we are wholly or partially rupturing the bonds between the atoms. In the scratch method some of the atoms are completely torn away from the main body. In the penetration method the atoms are permanently pushed aside from their normal space lattice. In the dynamic methods the distances between atoms are disturbed, thereby developing a certain strain which manifests itself in the reaction that helps produce the rebound of the hammer or the ball. This is not a permanent deformation. In all cases, however, we are dealing with interatomic forces. The closer and firmer the atoms stick together, the harder in general the material is said to be. The cohesive forces of materials are involved in hardness tests.

Relations Between Magnetism and Hardness

The author's assignment in the problem of hardness testing was to find relationships between magnetism and hardness as defined above. Certain relationships had been known, but no extensive knowledge was to be found on the subject. It was recognized, for instance, that certain degrees of hardness were more favorable for permanent magnets, and, therefore, remanence and coercive force were in some way related to the hardness. The Fröhlich-Kennelly equation gives

us one empirical relation: This equation is an expression for the function which reluctivity, (the reciprocal of permeability) is of the magnetizing force applied. Its form is:

$$\rho = a + \sigma H$$

where ρ is the reluctivity, a the coefficient of magnetic hardness and $1/\sigma$ is the saturation induction of the material.[3]

Having been interested in the subject of magnetostriction since 1907 it was natural that in looking for relations between magnetism and hardness, that the writer should turn to some possible correlation between the various magnetostrictive effects and mechanical hardness. Inasmuch as there are three types of magnetostrictive effects involving the three moduli of elasticity, it will at once be seen that there were some grounds for making comparisons between magnetostrictive effects and mechanical hardness.

Description of Magnetostrictive Effects

In the Joule magnetostrictive effect there is a change in length due to a longitudinal magnetic field. A magnetic field will thus permanently set up strains in ferromagnetic substances. It is apparent that in general this will be influenced by just the factors which affect hardness, viz., the cohesive forces. Young's modulus is affected by a longitudinal magnetic field.

In the Wiedemann magnetostrictive effect a twist of a ferromagnetic rod occurs, if a longitudinal and circular magnetic field are simultaneously imposed. Such a combination of fields influences the coefficient of rigidity. In the twisting of a steel rod due to the combination of a circular and a longitudinal field, interatomic forces are brought into play and must bear some relation to mechanical hardness.

In the Barrett effect a magnetic field changes the volume of a ferromagnetic substance. The bulk modulus is thereby influenced. Once more we may surmise that magnetostriction and mechanical hardness are closely allied. So far as this study is concerned, only one magnetostrictive effect will be considered, viz., the Joule magnetostrictive effect which will hereafter be referred to as the Joule effect. The Wiedemann effect is a special case of the Joule effect, because the resultant field of a longitudinal and circular field is a helix. A change in length along this helix means a twist of the rod.

[3]Spooner, "Properties and Testing of Magnetic Material," 1927, p. 362.

Fig. 1 illustrates this. Furthermore, the change in volume due to a magnetic field follows from a change in length longitudinally which is not completely compensated by the change in length which occurs at right angles to the direction of the field.

Application of the Joule Effect to Hardness Testing

In studying the Joule effect a ferromagnetic rod is placed symmetrically within a solenoid as shown in Fig. 2. As the magnetic field in the solenoid is increased from zero field, say, up to 1500

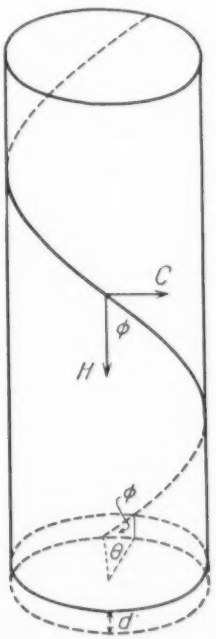


Fig. 1—In the Wiedemann Effect the Resultant Field Has the Direction of a Helix.

gausses, the rod will change its length. The way in which various ferromagnetic rods will change their lengths is shown in Fig. 3. Emphasis is laid upon ferromagnetic bodies in this study, because only ferromagnetic materials were employed. Kapitza[4] working with fields of great intensity finds that non-ferromagnetic bodies also change their lengths. If these relations between magnetostriction and hardness are real, then it would appear that the study may be extended to all classes of materials.

[4]Kapitza, *Proceedings* of the Royal Society, Vol. 131, 1931, p. 225.

Extensometer for Measuring the Joule Effect

For the measurement of these changes in length an extensometer[5] was devised by James T. Serduke, formerly with the General Electric Co. of Schenectady, N. Y. It has proved to be a very satisfactory instrument.[5] Fig. 4 shows the mechanism. It is a train of mechan-

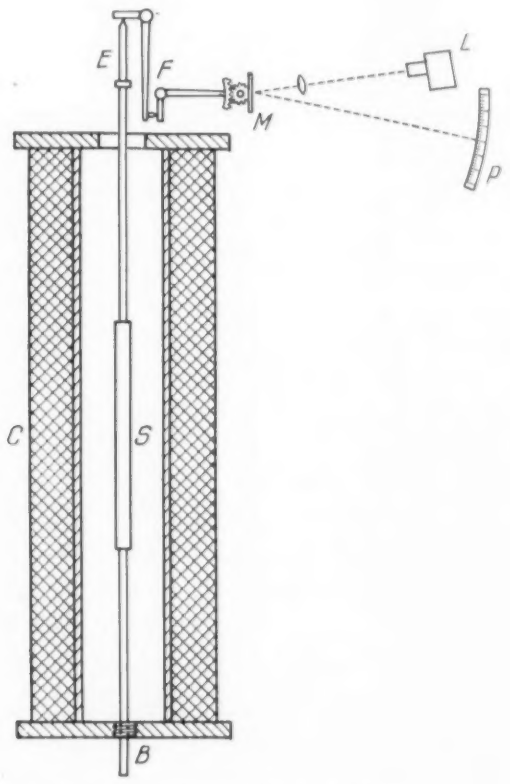


Fig. 2—The Ferromagnetic Rod S is Placed Symmetrically in the Coil C. As the Magnetizing Force of the Coil is Varied, S Changes its Length Which is Measured by the Extensometer at the Top of the Coil.

ical levers operating an optical lever whereby the changes in length may be multiplied. A light glass tube extends from the upper or free end of the rod in Fig. 2 and attaches to the lower end of E in Fig. 4. As the rod changes its length, E moves up or down and the lower end of the right angled lever F moving in or out, turns the train of wheels and so turns the mirror m. A very finely graduated screw fits into the extensometer as shown in Fig. 5. As its lower point P advances it comes in contact with F directly over the point to which

[5]Williams, Review of Scientific Instruments, Vol. 3, 1932, p. 675.

the rod E is attached. L is the lever by which the screw is turned. The angle through which the screw is turned is measured by the index I moving over the graduated scales. This gives a very accurate method for calibrating the extensometer. The movement of the

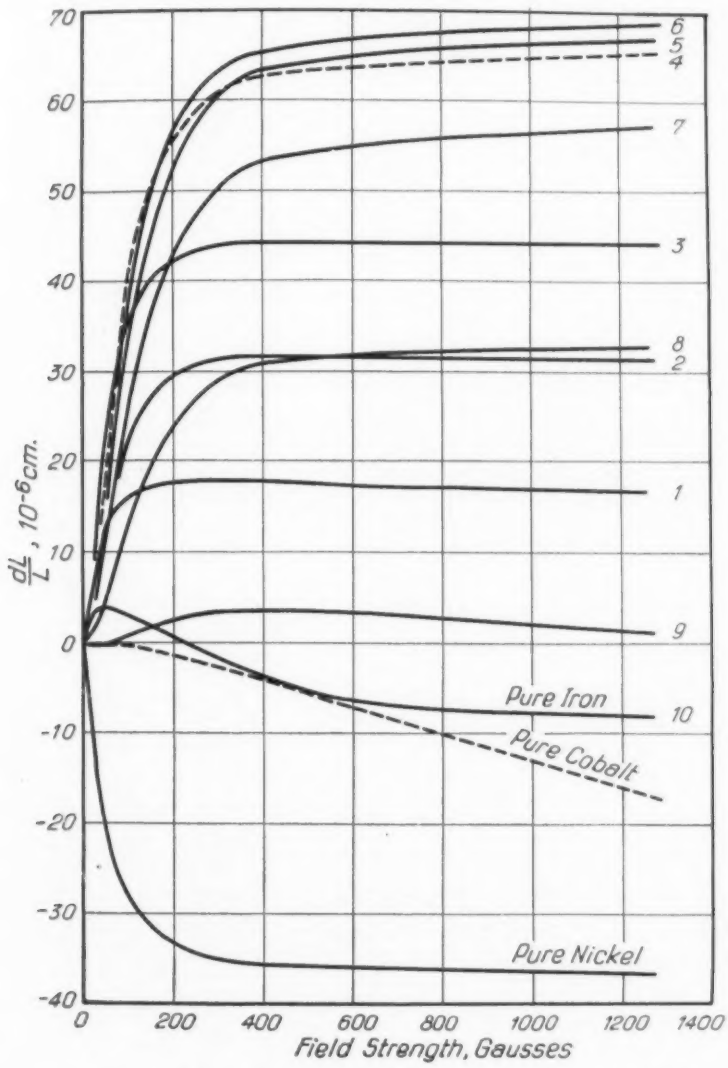


Fig. 3—Changes in Length of Various Ferromagnetic Rods When Magnetized Longitudinally. Alloys of Iron and Cobalt.

beam of light reflected by the mirror may be observed by a telescope and scale or it may be allowed to fall on a recording film camera like that shown in Fig. 7. An incandescent lamp with a straight filament is used as a source of light. This is placed in a vertical position and the image of the filament reflected from the mirror m

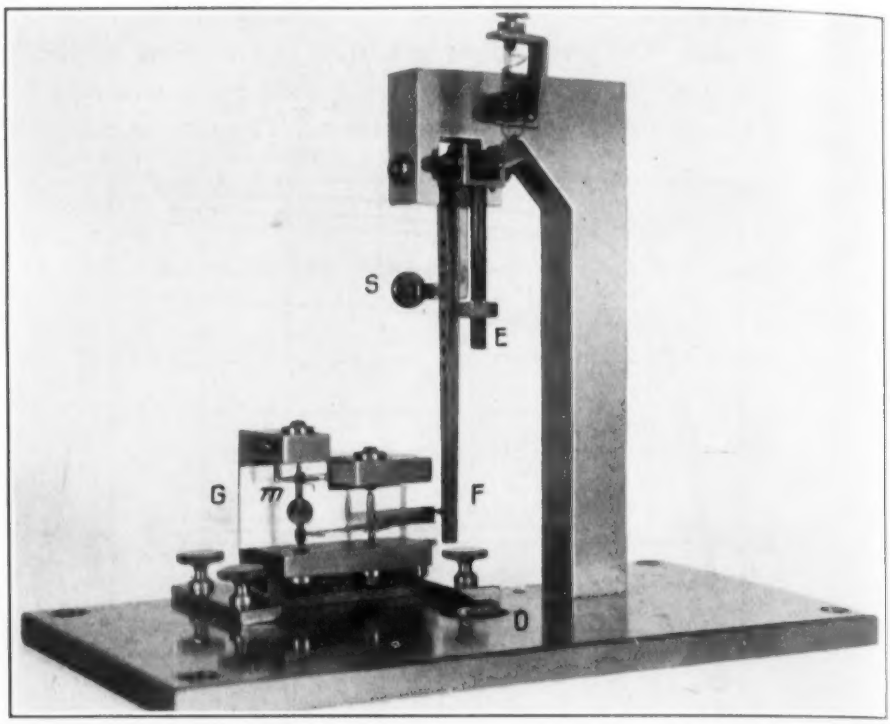


Fig. 4—An Extensometer Used in Measuring the Changes in Length of Ferromagnetic Rods When Magnetized Longitudinally.

falls on the horizontal slit (s, Fig. 6) of the camera. The slit replaces the lens in an ordinary camera. The image of the vertical filament being at right angles to the slit, the movement of the image in a horizontal plane throws a fine pencil of light through the slit. If the film moves in a direction normal to the slit, a trace is formed on the film like that in Fig. 7, which is the change in length for soft iron. The vertical lines represent the currents, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 3.0 and 5.75 amperes for the right hand record. While the left hand record omits 0.1, 0.2, 0.3 and 0.4 amperes respectively, flowing through the solenoid. Knowing the constant of the solenoid (128.5 gausses per ampere), the film records the deflections for various magnetic fields as the current is increased from zero. These values may then be plotted in a curve as shown in Fig. 3.

Ways in Which the Hardness of Ferromagnetic Rods may be Varied

With the above procedure of study in mind, attention is next turned to a study of the various methods for producing different

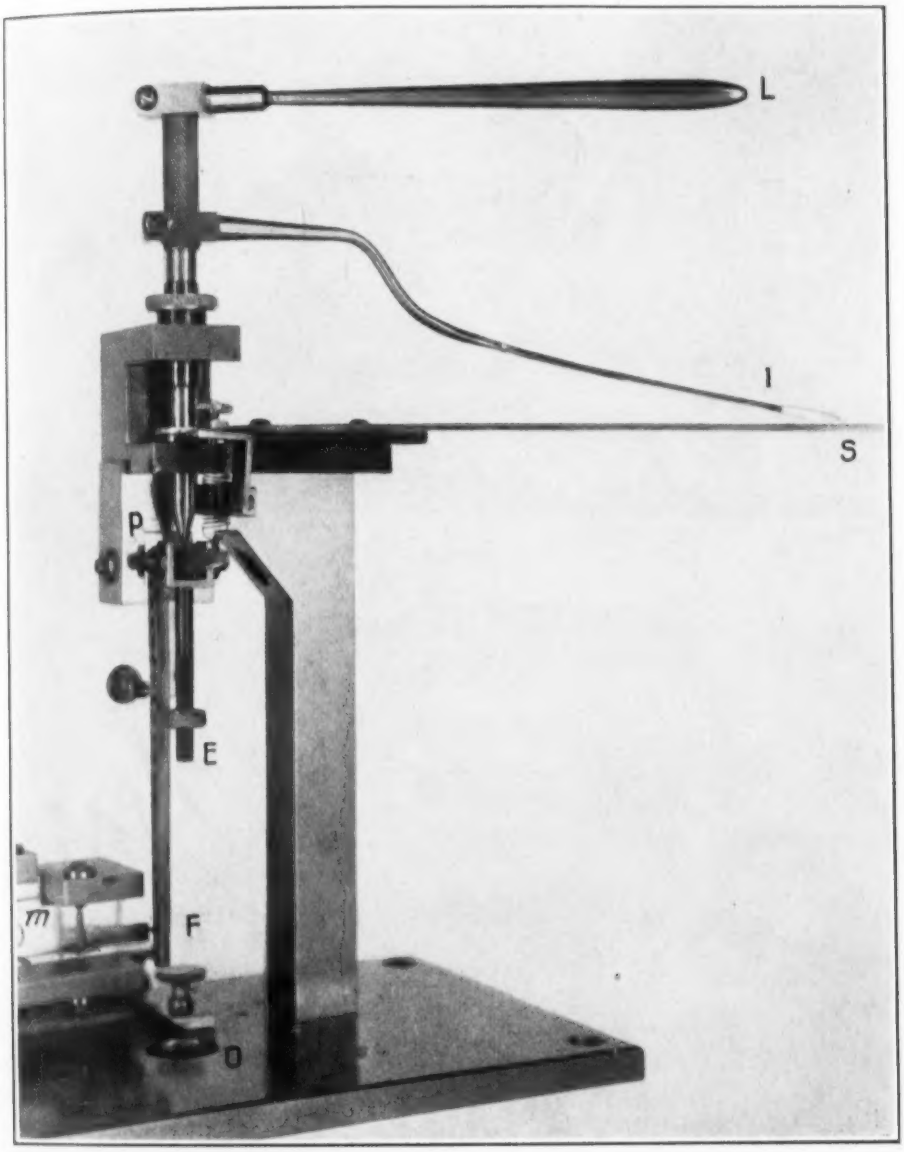


Fig. 5—The Screw Used in Calibrating the Extensometer.

degrees of hardness. There is hardness due to heat treatment, hardness due to cold working, hardness due to aging, and hardness secured by varying the chemical composition. In this particular study this last variation in hardness was obtained in a series of steel rods by varying the carbon content, other elements being approximately the same and they all had the same heat treatment.

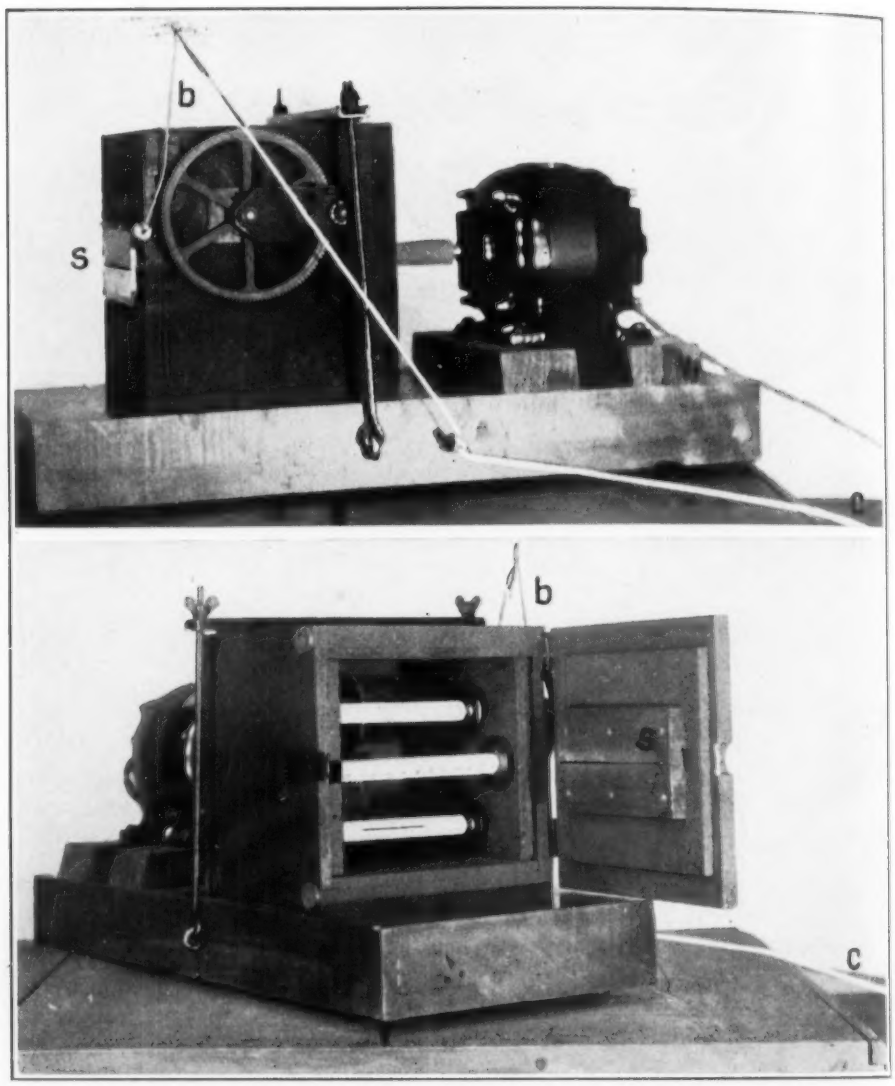


Fig. 6—Film Camera Used in Recording the Changes in Length of Ferromagnetic Rods. The Film is Moved Past the Slit and by a Reducing Gear Driven by a Small Electric Motor.

Hardness Varied by Tempering

The first study was made on a group of five rods whose hardness was varied by drawing at different temperatures. Table I gives considerable information regarding their chemical and physical characteristics.

The changes in length which these rods underwent as the magnetizing force was increased from zero up to 1000 gausses is shown

Table I
Chemical Analysis, Heat Treatment and Hardness

Rod No.	Carbon	Manganese	Phosphorus	Sulphur	Silicon
1	1.34	0.37	0.010	0.018	0.13
3	1.27	0.27			
4	1.23	0.32			
5	1.35	0.35			
6	1.27	0.37			

Heat Treatment

Rod No.	Tempering Temperature		Time
1	Not tempered (Used as Quenched)		
3	705 degrees Cent.	1301 degrees Fahr.	15 mins.
4	427 degrees Cent.	800 degrees Fahr.	15 mins.
5	565 degrees Cent.	1049 degrees Fahr.	15 mins.
6	705 degrees Cent.	1301 degrees Fahr.	2 hrs.

All specimens were oil quenched at 788 degrees Cent. (1450 degrees Fahr.)
Tempering—All specimens were air-cooled

Scleroscope Hardness (Average of Ten Readings)

Rod No.	Scleroscope Numbers
1	70.7
3	34.6
4	51.9
5	42.8
6	30.8

Common Diameter = 0.555 cm.
Common Length = 24.5 cm.

in Fig. 8. Rod 6 is not included because it was reheated two hours and not for just fifteen minutes as 3, 4 and 5 were. It will be seen from Fig. 8 that the softer the rod the greater is the positive elongation of the rod. This is shown to better advantage in Fig. 9 where

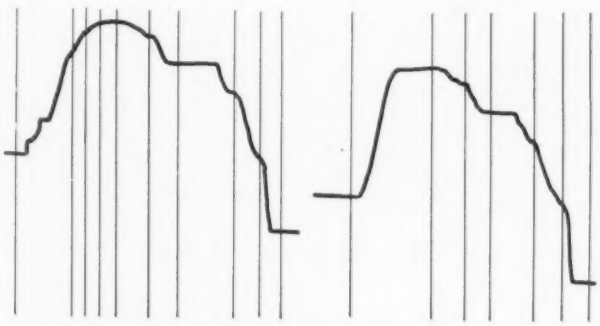


Fig. 7—A Continuous Record of the Change in Length of Armco Iron as the Magnetizing Force is Increased From Zero. Film Moves From Left to Right.

the maximum elongation is plotted against scleroscope hardness. In Fig. 9, rod 6 is included. From this curve it appears that rod 6 would lie on a curve below that for rods 1, 3, 4 and 5. This is confirmed by Rawdon and Epstein[6]. Wherein they showed that increase

[6]Rawdon and Epstein, Scientific Papers, Bureau of Standards, Fig. 18, p. 406.

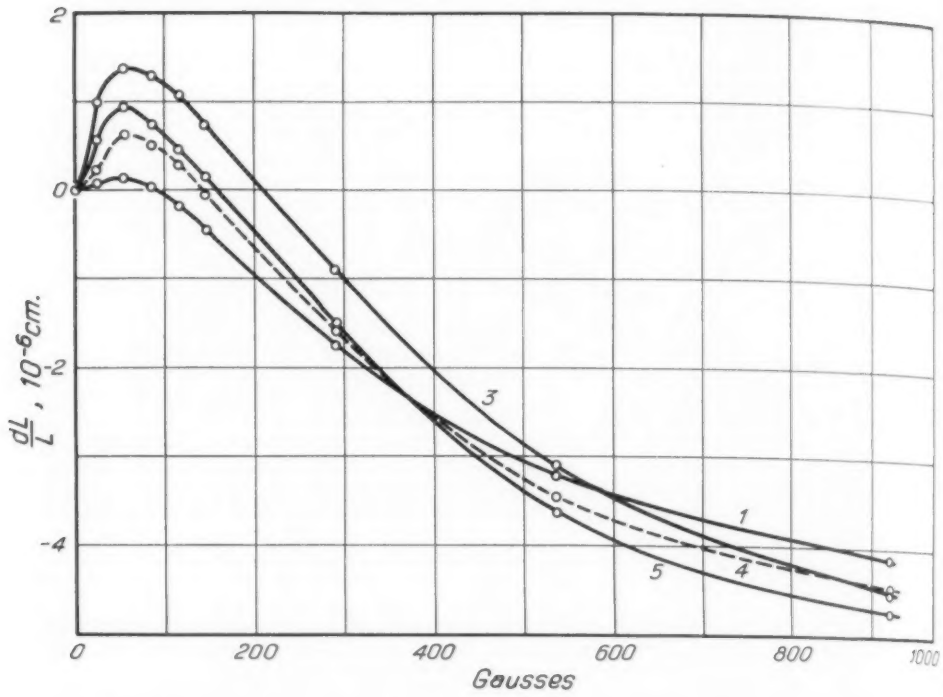


Fig. 8—Change in Length of Steel Rods, Whose Hardness Was Varied by Different Drawing Temperatures.

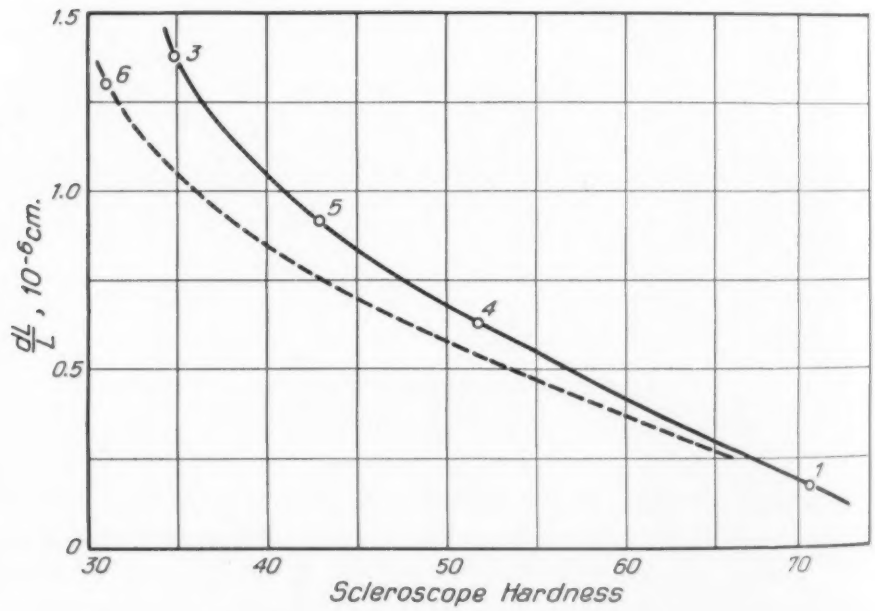


Fig. 9—Maximum Elongations in Fig. 8 Plotted Against Scleroscope Hardness.

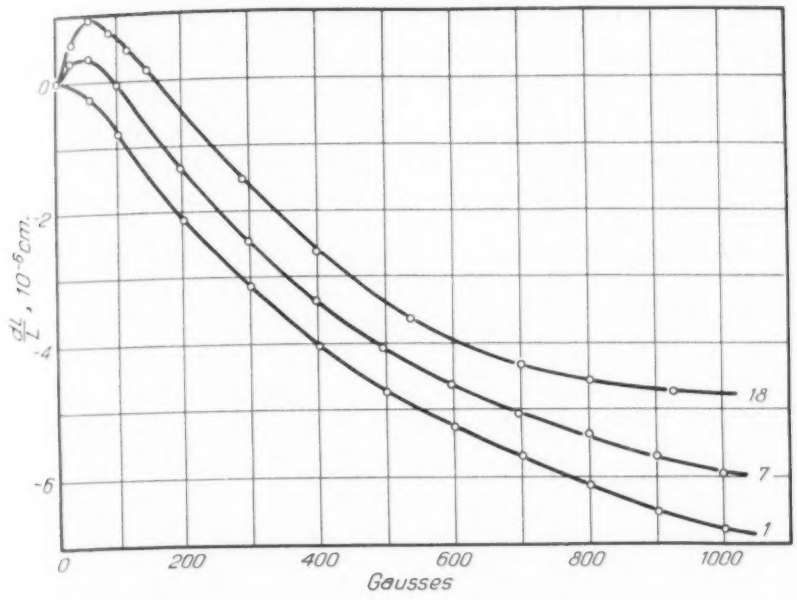


Fig. 10—These Curves Show How Rod 5 Progressed in Getting Softer From the First to the 18th Time it was Remagnetized.

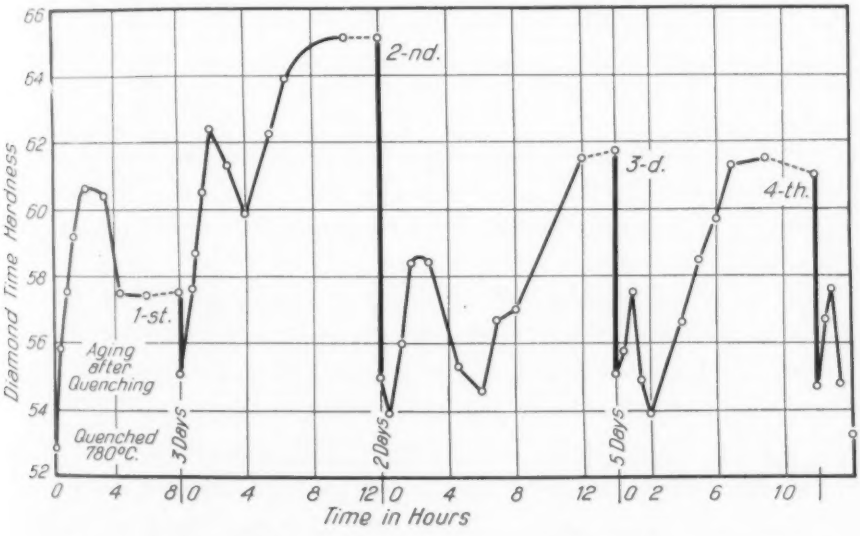


Fig. 11—Steel (0.76 C, 0.59 Mn, 0.15 Si) Quenched From 780 Degrees Cent.; Aged 1¼ Turn in Magnetic Field, Cold, Repeated Four Times.

in the time of tempering decreased the hardness. A set of rods given the same drawing temperatures as 1, 3, 4 and 5, but reheated for two hours would presumably lie on a curve shown by the dotted line in Fig. 9.

What seems to be a very remarkable effect was found in rod

5. For the first series of observations on this rod it did not have an initial lengthening, but with each succeeding run of observations, this initial lengthening increased until it became stabilized at the values shown in Fig. 8. Fig. 10 shows how this initial lengthening seemed to be pumped up by the reversals of the magnetic field. The stable state appeared to be reached after the rod had been put through 15-18

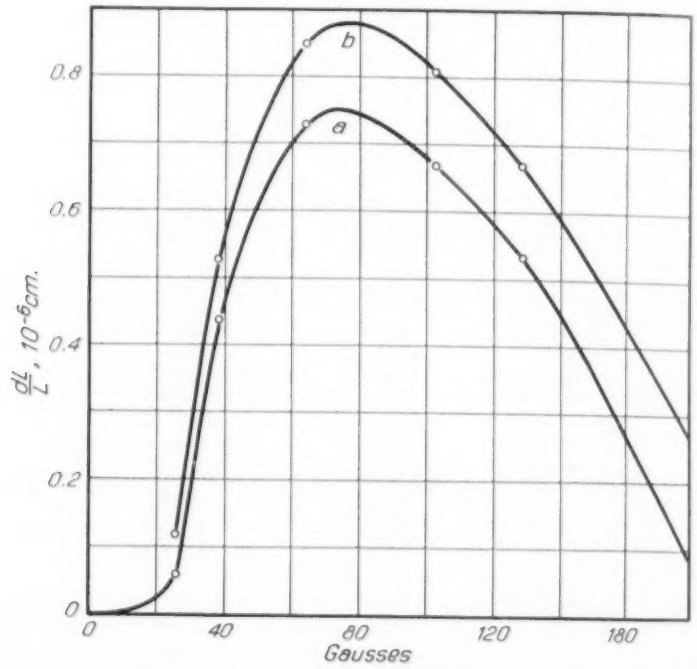


Fig. 12—Rod 5 is Softened by the First Reversal of Magnetization.

cycles of first a magnetization, then a demagnetization by an A. C. in the solenoid and then remagnetization in the opposite direction. Each series of observations followed one after the other as rapidly as they could be taken. According to the curves in Figs. 8 and 9, the maximum elongation was for the softest steel rod. An interpretation of the results shown in Fig. 10 would be that, as the reversals of the magnetic field piled up on rod 5, a softening process was going on in the rod. These observations were first made in 1922 and attention was called to the facts observed at that time,[7] but other lines of investigation led away from this point. Recently, however, it has taken on new significance from the work first published by Herbert[8] in 1929 in which he shows that the process of magnetization and

[7]Williams, TRANSACTIONS, American Society for Steel Treating, Vol. 5, April, 1924.

[8]Herbert, Iron and Steel Institute, No. 2, 1929, p. 239.

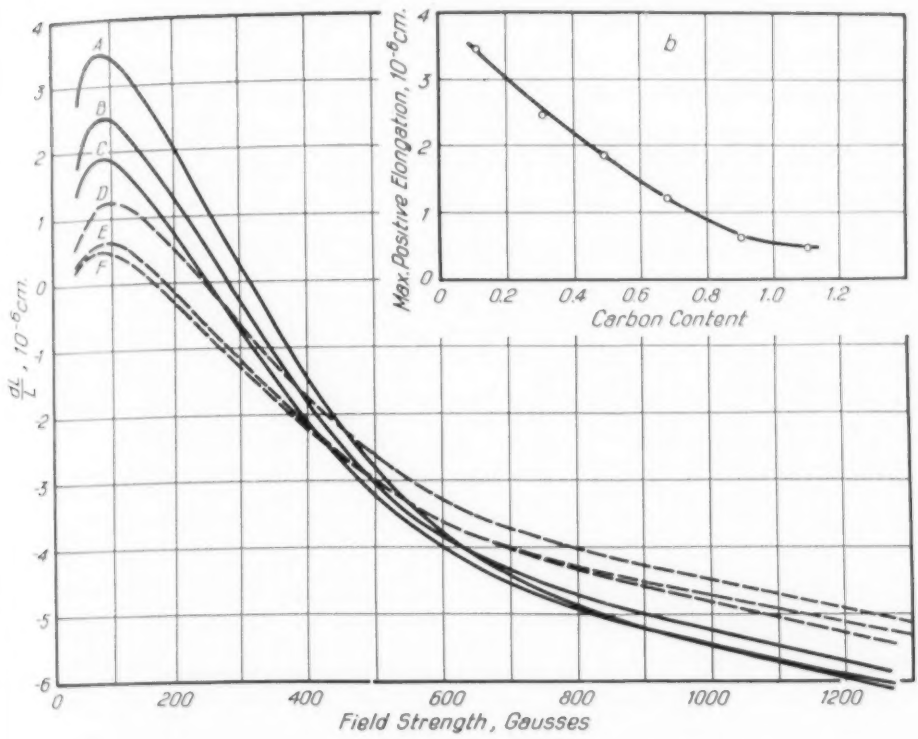


Fig. 13—Change in Length of Steel Rods With Different Carbon Contents.

reversal does change the hardness of steel and in a way which confirms the work of 1922. Fig. 11 shows a curve taken from Herbert's article. Each time he reverses the magnetism of the specimen, a softening occurs which is then followed by an aging process in which after the lapse of some hours the metal becomes harder.

In 1922 it was not observed that the rod 5 became harder by an aging process after being magnetically treated. Assuming that in ten years the rods had become fairly stable, they were brought out again and studied. This time the question of hardening by aging was considered. If the rods have hardened by aging since 1922 then the maximum elongation for the first application of the magnetic field should be less than for the second or successive applications of the magnetic field reversed. It must be remembered that the very process by which hardness is being studied also affects the hardness. To a certain extent this is true of many of the modern methods. In the static penetration method, as the ball sinks in, it changes the hardness at the point measured. Using rod 5 again, its changes in length

due to a magnetic field was measured without any previous magnetization. The change in length at the point of maximum elongation was that shown in (a) Fig. 12. On demagnetizing by a decreasing A. C. current in the solenoid and then observing the change in length when magnetized in the opposite direction, the values given in (b) Fig. 12 were obtained. This was repeated with various sorts of rods and similar results were obtained. The results were repeated for rod 5 after several days had elapsed and again similar results were obtained. The repetition was a duplication of the curves shown in Fig. 12. Herbert showed in his work that after 3 to 4 hours the hardening due to aging had been pretty well established. Both the work of 1922 and the work this year seem to fit in precisely with the observations of Herbert.[9] In the preparation of this paper an article by Matuyama has appeared in which he says he has not been able to corroborate any of Herbert's work. Other engineers in this country state that using static indentation methods they have not been able to verify Herbert's discoveries. In a private letter from Herbert, we learn that investigators in Germany are confirming his work. It leaves the problem in a curious position. It indicates the need for extensive studies along every conceivable line, for if there is any verity to the observations, they appear to be dealing with fundamental atomic theories.

Different Degrees of Hardness with Varying Carbon Content

While not the next step, historically, in this study it would be logical to take up a study of six steel rods whose hardness was varied by having different carbon content. Their heat treatment has been identical. In this series of rods there are 60 steel rods, 10 specimens to each value of carbon content. The purpose is to give these rods different heat treatments later when a more complete study is made of their magnetic properties as they now stand.

Although these rods had the same heat treatment, (they were hot-rolled and allowed to cool without interruption on the cooling beds), the six classes having different carbon contents showed marked differences in their hardness numbers. Table II gives some of the essential characteristics of these rods. They are lettered A, B, C, D, E and F respectively.

[9]Herbert, *Proceedings* of the Royal Society, Vol. 130, 1931, p. 514: *Metallurgia*, May and June, 1931.

Table II

Rod	Carbon	Manganese	Phosphorus	Sulphur	Rockwell Hardness
A	0.11	0.49	0.010	0.039	64.2
B	0.31	0.53	0.012	0.039	77.1
C	0.49	0.41	0.012	0.033	83.4
D	0.69	0.48	0.019	0.033	94.5
E	0.91	0.44	0.023	0.027	97.3
F	1.11	0.42	0.019	0.036	99.9

These rods were 0.645 centimeters in diameter and 24.5 centimeters in length. Fig. 13 shows how the change in length varies as the field is increased from zero up to 1250 gausses. The maximum lengthening progresses with the softening of the steel rods which in

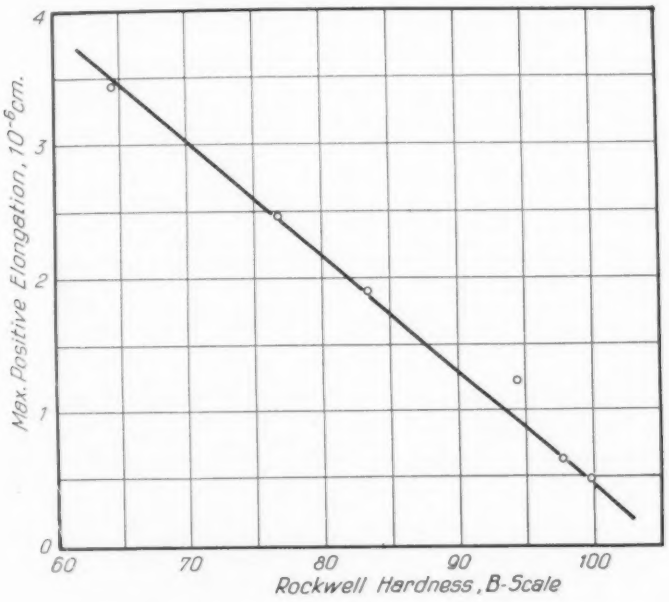


Fig. 14—The Maximum Elongations of the Curves in Fig. 13 Plotted Against Hardness Numbers.

turn largely follows the carbon content. These relations are shown in (b), Fig. 13 and in Fig. 14. Once more the values of the maximum elongations are seen to be a measure of hardness for this second method for changing the hardness. Again the test was made to see if in this latter kind of hardness there was a softening due to reversal of magnetization. Fig. 15 shows that softening follows a reversal of the magnetic field. The values shown in the two curves are for the rod D.

For many years the writer has been impressed with the fact

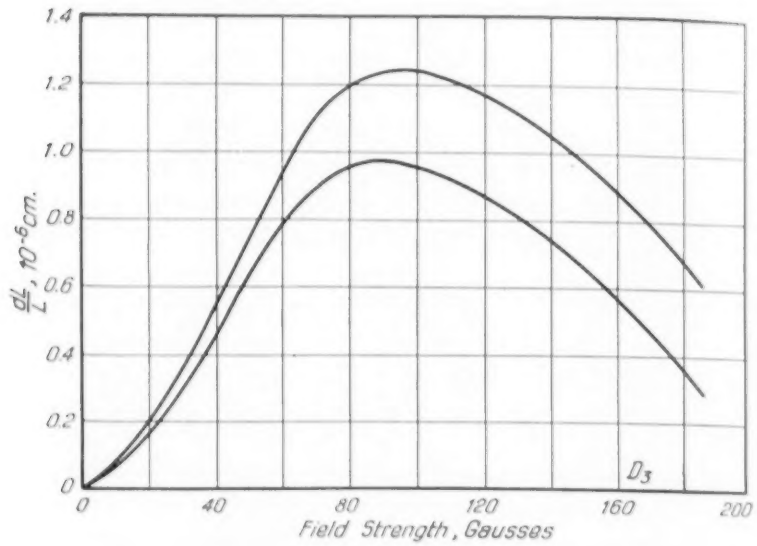


Fig. 15—Rods, With Hardness Varied by Different Carbon Content, Also Show Softening by Reversal of Magnetization.

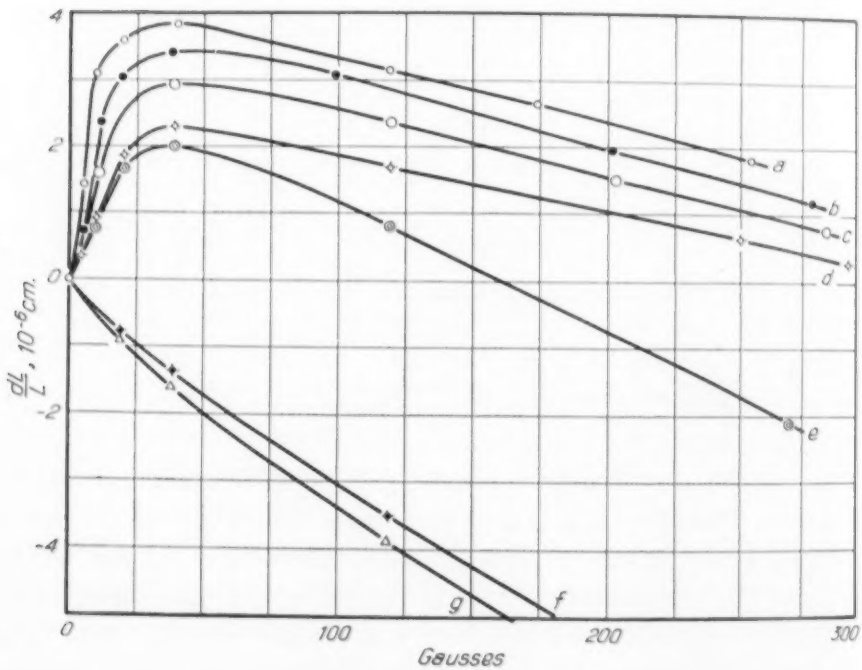


Fig. 16—Change in Length of Steel Rods in a Magnetic Field as They are Reduced by Cold Working to Smaller and Smaller Sizes.

that it was impossible to repeat results with the accuracy that was assumed should be possible with the extensometer used and the care taken in temperature control. In large part the annealing process due to reversal of magnetization will account for this lack of uniformity of results, for we see here a variation of something like 10 per cent in some cases. Furthermore this occurs for both kinds of hardness thus far studied.

Cold-Worked Metals

Change in hardness may also be produced by cold working. The next set of material which should be tested is a group of rods or strips of steel whose hardness has been varied by cold rolling or cold

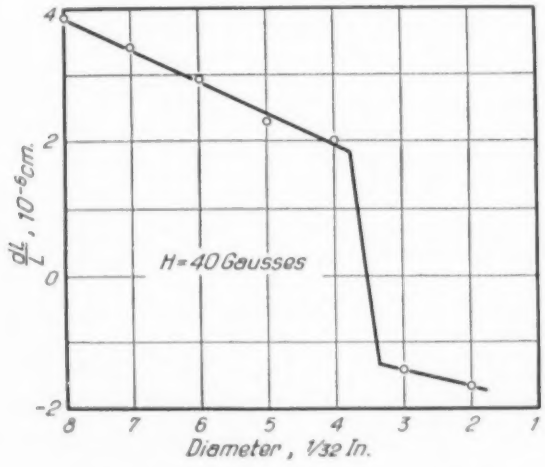


Fig. 17—The Changes in Length, for the Rods of Fig. 16 at a Common Field Strength of 40 Gausses, are Here Plotted Against Reduction by Cold Working.

drawing. Thusfar in this study no such group of steel specimens has been studied, but fortunately Rankin[10] has studied the Joule effect in a series of cold drawn rods. His results appear to fit in with the work thusfar described. His wires or rods varied in diameter by $\frac{1}{32}$ of an inch, the thickest being $\frac{1}{4}$ inch and the thinnest $\frac{1}{16}$ inch diameter—the reductions in diameter being achieved by cold drawing on the same original material. Fig. 16 shows the changes in length for these seven different sized rods which it is assumed were made harder and harder as they were reduced in size by cold working.

[10]Rankin, *Journal* Royal Technical College. Glasgow, p. 587, Jan. 1932.

Here again the maximum values of the positive elongations are a measure of the hardness of the rods until for the last two there seems to have been a violent change in the structure of the wires, and no positive elongation occurs. "Hardness and strength of a metal increases with the amount of reduction by cold work until internal

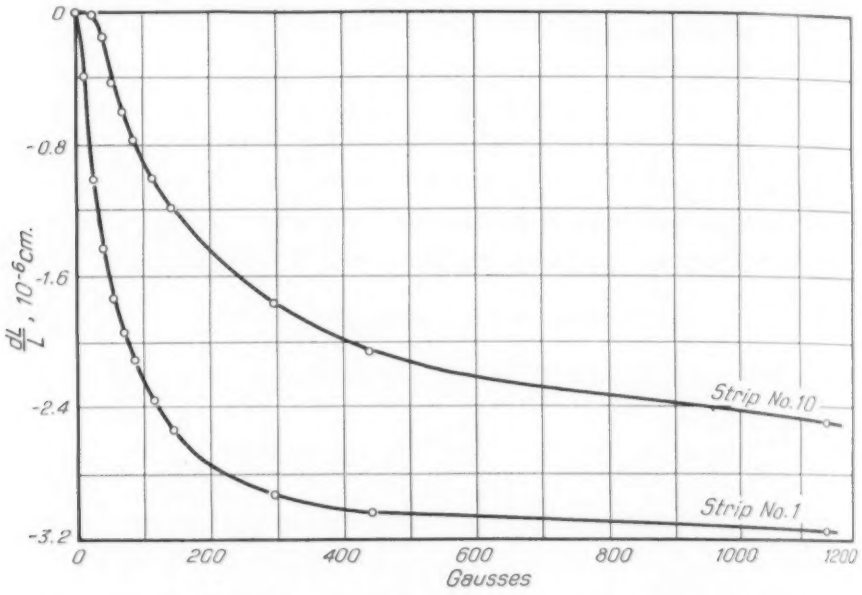


Fig. 18—The Shortening of Nickel Rods in a Magnetic Field with Different Degrees of Hardness.

failure is produced."[11] One may assume that so far as the magneitc test is concerned the two samples f and g have passed this point. In Fig. 17 the change in length for these rods at a field strength of 40 gausses is plotted against reduction in diameter. This is roughly against increasing hardness.

Work has been done, however, on two series of ferromagnetic rods whose hardness has been varied by cold rolling. These two series were of nickel and of monel metal respectively.

Nickel Strips—Referring to Fig. 3, it will be noted that nickel shortens for all field strengths and has no elongation peak as did the steel rods which have just been examined. It was of interest therefore, to see how the change in length would vary with the hardness in metals which did not possess these positive peaks of elongation. At the same time it was of interest to study the Joule effect in metals hardened by cold rolling.

[11]Jeffries and Archer, "The Science of Metals," p. 201, 1924.

The strips of nickel were prepared as follows: eleven strips 2 inches wide, ¼ inch thick and about 3 feet long were annealed under the same heat treatment. One strip was left as annealed and the other ten were then reduced by cold rolling to various percentages of reduction. The essential characteristics of these strips are given in Table III.

Table III
Cold-Rolled "A" Nickel Strip

Strip No.	Scleroscope No. (Universal Tup or Hammer)	Percentage Cold Reduction
1	17	0
2	27	9.7
3	31	18.9
4	35	28.9
5	40	39.5
6	43	50.0
7	45	59.5
8	47	69.0
9	50	79.0
10	51	89.1
11	49	93.3

Chemical Analysis

Nickel	98.88
Copper	0.16
Iron	0.56
Sulphur	0.008
Silicon	0.06
Carbon	0.09
Manganese	0.23

After these strips were received they were cut in two lengthwise and trimmed to a width of ⅜ inch, the thickness being that given in Table III. The common length was 24.5 centimeters. The cutting and trimming was done slowly in order to avoid heating and thus change the mechanical properties. Local strains were released by heating the strips for one hour at a temperature of 570 degrees Fahr. in an oil bath. With two samples from each specimen of nickel it was possible to check the results of one with those of the other. This gave 22 specimens to be measured. They were lettered as follows:

$$A_1,\ A_2,\ A_3, \ldots\ldots A_{11}$$
$$B_1,\ B_2,\ B_3, \ldots\ldots B_{11}$$

respectively in which the subscripts correspond to the strip numbers in Table III. All of the strips showed the shortening for all field strengths which is characteristic of nickel shown in Fig. 3. Fig. 18 shows how two of the rods changed their length. These are

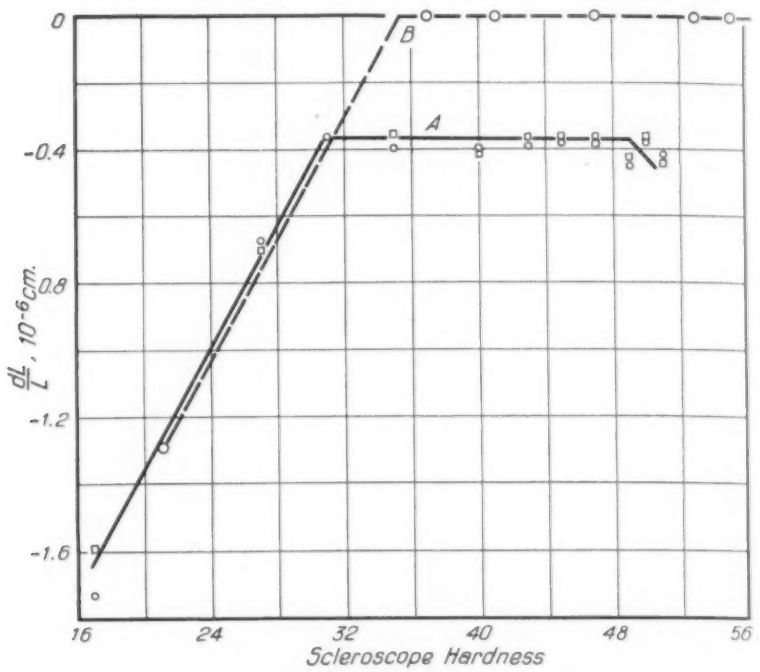


Fig. 19—Curve A Shows the Way in Which Nickel Rods Change Their Length in a Magnetic Field as the Hardness Varies. Curve B Shows the Changes in Length of Monel Metal Rods at a Common Field Strength of 400 or More Gausses, Plotted Against Hardness.

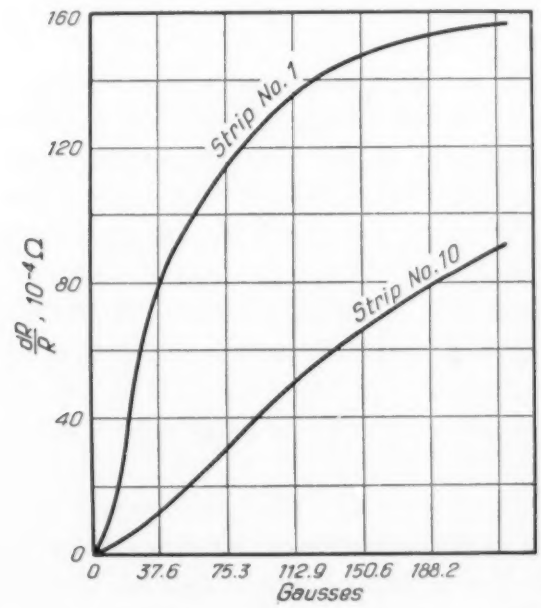


Fig. 20—The Nickel Rods Used in Fig. 18 Show Increase in Resistance as the Magnetizing Force is Increased.

the extremes of the series. If one choses a common field strength and plots the values of the shortening of the various rods at this field strength it will be seen how they vary with different degrees of hardness. This is shown in Fig. 19 where scleroscope hardness is

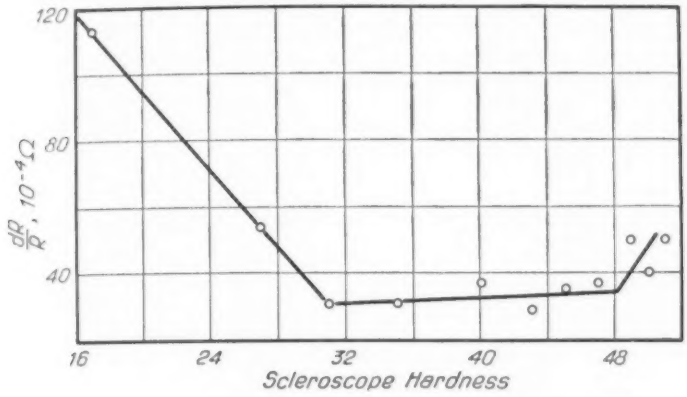


Fig. 21—A Series of Nickel Rods Shows Changes in Resistance at a Common Field Strength of 75.3 Gausses, Analagous to the Changes in Length Shown in Fig. 19.

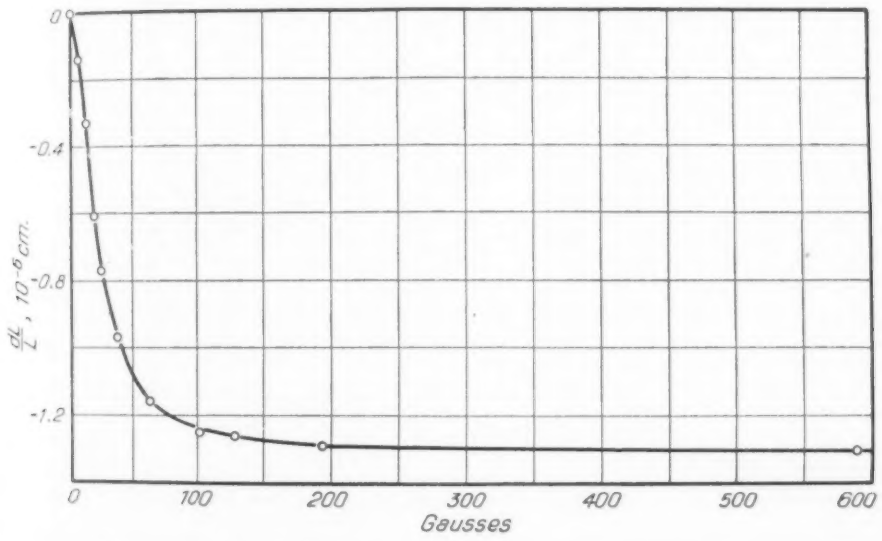


Fig. 22—Monel Metal Changes its Length by Shortening for all Field Strengths.

taken as the abscissa and 58.8 gausses as the common field strength. The outstanding fact to be deduced from this study is that, after the first two reductions of the strips by cold rolling, the machinery in the rods whereby change in length occurs is reduced to a common phase, unless it turns out in further study that at the tenth reduction

things begin to break up again. It will be seen in Fig. 19 that there is some indication of this possibility. Unfortunately the percentage reduction did not go any farther in this series of nickel strips.

Very closely allied with the magnetostrictive effects is the change in electrical conductivity with change in magnetization along the direction in which the current flows. If one measures the

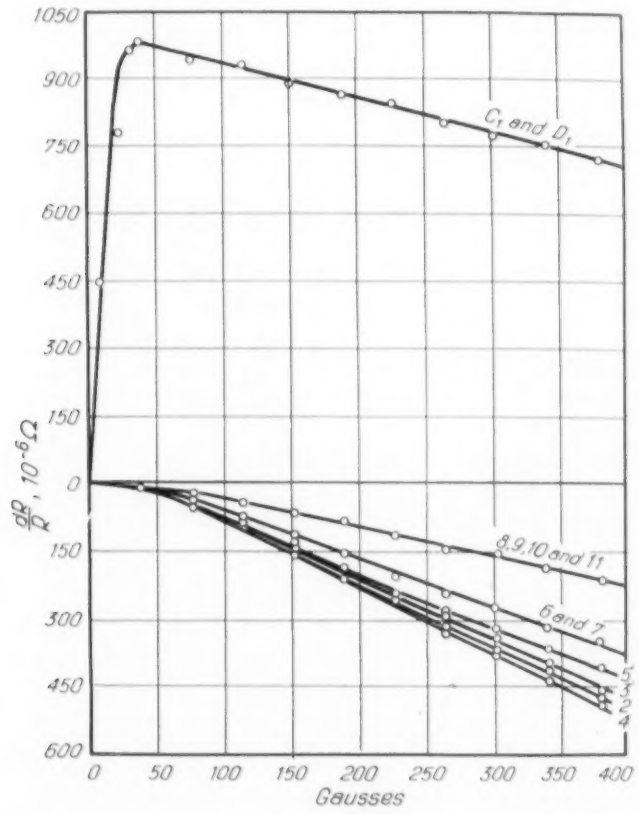


Fig. 23—Monel Metal Increases Its Resistance in a Magnetic Field When Annealed, But Decreases it When Cold Worked.

changes in resistance of this same series of nickel strips and plots the same against the hardness of the various rods he gets a curve surprisingly like the curve shown for changes in length in Fig. 19. See Fig 20. Fig. 21 gives the change in resistance per ohm for the strips at the common field strength of 75.3 gausses as a function of the hardness.[12] Increasing the hardness reduces the change in resistance produced by a longitudinal field. The same machinery seems to be involved in the change of resistance due to a magnetic field that is

[12]Williams and Sanderson, *Physical Review*, Vol. 37, 1931, p. 309.

instrumental in causing the changes in length of the ferromagnetic substances.

Monel Metal—Monel metal, an alloy of copper and nickel, loses its ferromagnetic properties around the boiling point of water. A set of cold-rolled strips of monel metal were prepared in the same way as was the series of nickel strips. There were 22 of these strips whose essential characteristics are given in Table IV.

Table IV
Monel Metal

Sample No.	Thickness In Inches	Scleroscope Hardness Univ. Tup or Hammer	Per Cent Cold Reduction
1	0.255	21	0
2	0.094	37	63.1
3	0.090	41	64.7
4	0.079	47	69.0
5	0.070	53	72.6
6	0.059	54	76.9
7	0.048	54	81.2
8	0.039	55	84.7
9	0.030	55	88.8
10	0.020	55	92.2
11	0.010	55	96.1

Chemical Composition:

Copper	30.20
Nickel	66.07
Iron	1.83
Sulphur	0.033
Silicon	0.03
Manganese	1.59
Carbon	0.23

It will be noted that the first reduction is greater than that accomplished in the first seven for the nickel strips. In some ways it was unfortunate that so large a step was made in the first reduction. The 22 samples were designated as follows

$$C_1,\ C_2,\ C_3, \ldots\ldots C_{11}$$
$$D_1,\ D_2,\ D_3, \ldots\ldots D_{11}$$

where the subscripts correspond to the sample numbers in Table IV.

Fig. 22 is the resultant curve for C_1 and D_1 showing how monel metal for that particular degree of hardness changes its length as the magnetizing force is increased from zero up to 650 gausses.[13] The curious result obtained on the rest of the rods was that there were no changes in length due to a magnetic field although the extensometer was arranged to measure a change in length of 1×10^{-8} centimeters. The entire machinery for changing the length by a magnetic field has been completely broken down by cold working,

[13]Results by H. H. Smith, not yet published.

i.e., by a 63 per cent or more cold reduction. This is shown in Fig. 19.

Microscopic examination of the nickel strips showed that there is a crushing of the crystalline structure and a reduction of the grain size. In all probability a preferred orientation is given to the structure.

The change in resistance due to a longitudinal magnetic field was also studied. Fig. 23 shows the average change in resistance

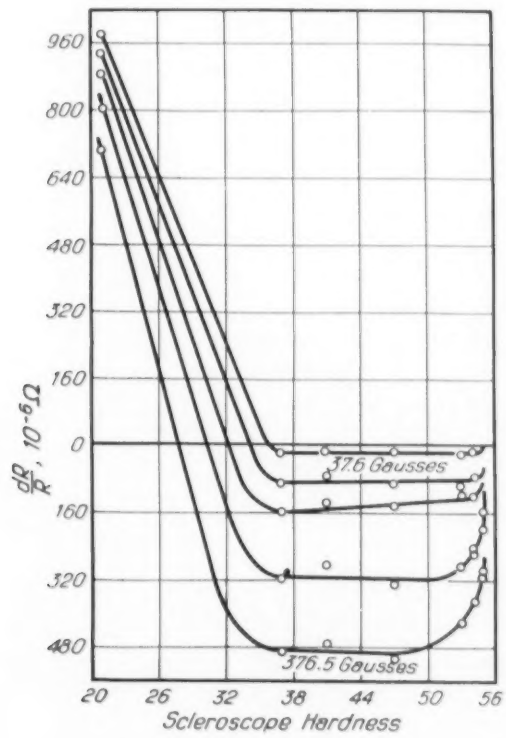


Fig. 24—These Curves Show the Changes in Resistance of Monel Metal for Various Degrees of Hardness at Common Field Strengths.

per ohm for the strips C_1 and D_1 as the field was increased from zero up to about 400 gausses. It follows quite closely the change in length for corresponding fields.

Whereas there was an increase in resistance for C_1 and D_1 there was a decrease in resistance for all the other strips. Unfortunately, the Kelvin double bridge, used in measuring the changes in resistance, although the resistance could be measured to one part in a million, was just able to detect this change. The results are

erratic, due no doubt to the very reason for which this whole study was made and therefore these results must be taken as merely qualitative.

Of the decrease in resistance of the monel metal strips for all of them except C_1 and D_1, there can be no doubt. The exact magnitude, however, is limited by the precision of the Kelvin bridge. Taking these values of the changes in resistance for what they are worth they are plotted in the curves shown in Fig. 24. Those rods having the same hardness numbers were averaged together. If these changes in resistance are now plotted against hardness numbers it will be seen that the resultant curves are not unlike the one shown in Fig. 21 for the nickel strips. The common field strengths chosen for these curves are indicated in Fig. 24.

Summary

The values of the maximum elongations of steel rods in a magnetic field are a measure of their hardness, other factors being kept constant. This holds for hardness developed by four different methods. Rankin's investigations indicate that even this fails to register hardness beyond a certain degree of percentage reduction. This point is confirmed by the cold working of nickel and monel metal. At a certain percentage reduction a sudden break appears in the relation between the changes in length and hardness numbers. See Figs. 17, 19 and 21.

The importance of this correlation between hardness and magnetostrictive effects lies in the hope that such studies will not only throw light on that property called hardness, but also give us some additional clues regarding the machinery which functions when a ferromagnetic rod changes its length in a magnetic field.

Grain size is a very important factor in changing the hardness of materials. There can be little doubt but that grain size has a great deal to do with the magnetostrictive effects also.[14]

This investigation appears to establish the fact observed in 1922-1923 that the hardness of a ferromagnetic body is reduced by reversing the direction of the magnetizing force applied to it.

The foregoing study has only touched the fringe of this problem. Studies should be made of grain size, Young's modulus, effects of greater reduction in cold working and scores of other points in

[14]Williams, *Science*, Vol. 66, 1927, p. 358; Vol. 65, 1927, p. 306. Sucksmith and Potter, *Nature*, Vol. 118, 1926, p. 730.

which correlations might be made with hardness. This study makes clear how important cooperative research is in such a problem and for the most part in all research. For this particular problem, a group of chemists, physicists, metallurgists and those competent to handle X-ray analyses could make a wonderful beginning on this important question.

In conclusion the author takes great pleasure in acknowledging his indebtedness for materials to Dr. H. L. Whittemore of the Bureau of Standards, to C. F. W. Rys of the Carnegie Steel Company, to Dr. P. D. Merica of the International Nickel Company and to Dr. W. E. Ruder of the General Electric Company.

ALLOY TOOL STEELS AND THE DEVELOPMENT OF HIGH SPEED STEEL

By Arthur S. Townsend

Abstract

This paper gives the history of alloy tool steels from 1868 to 1933 and traces the development of the various types of high speed steel. Much has been written on this subject but many statements in the literature are inaccurate and misleading. An effort is here made to establish the facts in regard to certain disputed points. Howe, Brustlein and many other workers in this field are given credit for important contributions. The parts played by F. W. Taylor and Maunsel White are discussed and an attempt is made to determine precisely what they invented.

METALLURGICAL literature contains innumerable references to the development of high speed tool steels, and to the fact that these steels were the successors of the so-called self-hardening steels. The complete and true story of this development, however, has never yet been published, and even today considerable confusion exists with regard to the differences between the various types of self-hardening and high speed tool steels. Although this confusion for many years was due largely to inadequate knowledge, it was increased in later years by certain attempts which were made to becloud the actual development. Some have tried to summarize the history briefly, and have made or have repeated inaccurate statements: a few have distorted the facts in order to prove a point they wished to make. The result is that certain errors have persisted, and probably still persist. In this paper an effort is made to present all the facts as fairly and as impartially as is possible under the existing circumstances.

Writers who deal with the history of high speed steel usually begin with "R. Mushet's Special Tool Steel," and state that this was the first of the self-hardening tool steels. This fact is well established. The steel was invented by Robert Mushet of England about 1868, and for twenty-five years or more it was practically the only

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tool steel in use other than unalloyed carbon steel. Its composition may have varied to some extent during the years up to 1900, but its type composition was roughly 2 per cent carbon, 2.5 per cent manganese, and 7 per cent tungsten. Although it often contained about 0.50 per cent chromium, and approximately 1.10 per cent silicon, these elements were of secondary importance, and the steel is properly classed as a manganese-tungsten steel. Table I (page 792) gives a number of analyses of this steel from seventeen different sources.

This steel possessed remarkable properties, some of them valuable and some of them just the opposite. These peculiar properties, as we now know, were due to the combination of the manganese and tungsten, together with the high carbon. True Mushet steels invariably had a high manganese content. As a consequence they were distinctly different from other types which had a low manganese content, and which were developed later. This distinction between types is important to any one who is tracing the history of this development, in fact it is essential to a clear understanding of some of the events. It was important also to the users of tool steels in the years 1895 to 1900 and later, because of its relation to proper heat treatment, but many of them did not realize this. At that time scientific knowledge regarding the various tool steels then coming into use was exceedingly limited and incomplete, and even the steel "experts" of that day probably did not understand the real points of difference and points of similarity between the various types.

Fred W. Taylor, in his voluminous report of 1906, showed that he was aware of the difference between the chromium-tungsten and manganese-tungsten types, (1)* but it is probable that even Taylor did not at the first fully appreciate how different in type the Mushet steel and some of its American competitors were. His extensive and thorough investigations finally brought to light the essential differences in chemical composition, as well as many other important points of these steels.

Obviously, a chief reason for the confusion at the beginning was the inadequate metallurgical knowledge of the period. In 1895 most of the alloy steels were either unknown, or were new products. Steel laboratories then were not very common, analyses when made were usually kept as carefully guarded secrets, and a science of metallography was practically nonexistent. It is not at all strange.

*The numerals appearing in parentheses pertain to the references appended to this paper.

then, that all air-hardening steels were frequently grouped together, without regard to the real distinctions existing between the various types of steels.

References to such steels were rare in the technical journals up to 1892, and a contribution from the pen of John W. Langley of Pittsburg which appeared in that year is therefore of special interest (*2*). It is likely that the function of the alloying elements was then imperfectly understood, so that Langley must be ranked as something of a pioneer in this particular field. He was one of the first, if not the first, to call attention to the fact that the addition of tungsten alone does not make steel "self-hardening." It must also be "excessively high in manganese and carbon." His paper was valuable because it provoked discussion as to the cause of air-hardening, and it may have stimulated other metallurgists to further investigations. It is interesting that Langley made brief mention of chromium steels as useful alloy steels, but did not mention chromium-tungsten steels. He was apparently unaware that chromium could be used in place of manganese, and in combination with tungsten would produce a second air-hardening steel. This discovery was to be revealed only a short time later.

As we look back we can now see that in the years 1894-1898, Mushet steel, up to that time supreme in its field, was at last beginning to encounter competition. It may be true that the new varieties of self-hardening steel were at first only imitations of Mushet, and that the purpose of the American makers was to make a steel "as good as Mushet," but it was soon discovered, at least by the most progressive of the makers, that some of the new steels were in some respects decidedly superior to the Mushet steel. The high manganese steels had certain inherent faults which prevented their more extensive use. It was practically impossible to anneal them or to machine them, and it was necessary to use great care in forging them on account of their red-shortness. The early chromium-tungsten steels showed promise of overcoming these defects to some extent, and their status as mere substitutes for Mushet steel gradually changed for the better. It is uncertain as to just how highly the newer steels were regarded; the best composition had not yet been determined, all sorts of compositions and qualities were on the market during this period, and no doubt some heats were much better than others. Among the more prominent American makers in this particular field were Crescent, Midvale and Sanderson.

For the sake of simplicity it is convenient to say that the air-hardening tool steels of 1898 were of three distinct types, manganese-tungsten, chromium-tungsten and chromium-molybdenum. Actually there were many variations in the types and also combinations of the types. Judging from the existing records of the composition of the tool steels of this period, (and we are principally indebted to Taylor for these) the early aim of the American manufacturers, up to 1893, was to make a good manganese-tungsten steel. Manganese varied from 1.80 to 2.70 per cent, tungsten was usually 6 to 8 per cent but occasionally as high as 11 per cent, with carbon 1.10 to 2.20 per cent. Although definite evidence on this point is lacking, it is probable that the American manufacturers at this time were beginning experiments with the air-hardening steels and were making more or less systematic attempts to modify and improve them. One modification, for instance, was the increase in chromium content from about 0.40 to 1.25 per cent or more. As used in some of the mills, this chromium at first was an addition to the manganese-tungsten steel. It was apparently not conceived of as a substitute element for the manganese, but was a further addition to a Mushet type steel. Eventually the chromium was increased to three or four per cent and the manganese was reduced to amounts no larger than are found in carbon tool steel, and this proved to be a very important forward step. Some manufacturers, however, were slow in making this change, and it seems quite probable that their reluctance to do so was because of their adherence to the theory that high manganese was an essential for a self-hardening steel.

When chromium began to be introduced as a useful constituent of tool steel, the high manganese content was retained by some makers, and the chromium was used as an additional element, so that the steels became carbon-manganese-chromium-tungsten alloys. The analysis of two such steels as recorded by Taylor is as follows:

	Tool No.	C	Mn	Cr	W	Si	Year Analyzed
Sanderson	79	1.84	2.43	2.69	11.59	0.89	1893
Jonas and Colver	73	1.85	2.33	2.96	10.72	1.03	1894

Tool No. 73 was said to be "very hard to forge and brittle in the body" (14). Such steels as these, however, had a comparatively short trial. The type that finally won out and displaced all others proved to be the chromium-tungsten type with low manganese (about 0.35 per cent manganese). In other words, chromium replaced man-

ganese as the element that combined with tungsten and carbon to give air-hardening properties.

It was of course the brilliant work of Taylor and White that brought about the supremacy of the chromium-tungsten type. They discovered the high heat treatment and showed the great possibilities of the chromium-tungsten type steel when treated by this process. Without their work, the adoption of the chromium-tungsten and the superseding of the manganese-tungsten type, would not have come so soon. We can guess, however, that it would have come eventually, although probably much more slowly, but the trend was in that general direction.

At this point we come to the question of the real origin of chromium-tungsten steels. Who was responsible for their invention and their adoption as tool steels? Since this subject is so closely interwoven with the history of the simple chromium steels, it is advantageous to recall briefly certain facts with regard to these early alloy steels. Julius Baur of New York is credited with being the first to make chromium steels commercially. He took out patents for manufacturing such steel in 1865. The early chromium steels as a rule contained less than 1 per cent chromium. They were used as construction steels primarily, and not as tool steels. From their earliest use up to about 1890, it appears that these steels were received with considerable skepticism by the metallurgical world. About 1873 it was widely advertised by the manufacturers of the steel that the great new bridge at St. Louis, Mo., was constructed with chromium steel. A little later it was shown that steel samples taken from this bridge contained only small percentages of chromium, less than half of one per cent, and indeed some samples contained no chromium at all. For a period of a few years chromium steels fell into disrepute. The great metallurgist Henry M. Howe writing on the status of chromium steel in 1887, refers to the fact that many users had been greatly disappointed with it (3). He concludes by stating that he is confident it is entitled to a far better position than it had acquired.

During this same decade, 1880-1890, considerable experimentation with chromium steels was being carried on in France. Henri Brustlein, of the Holtzer Steel Works, was the metallurgist in charge of these experiments. The chief interest of the French steel company in the chromium steels was probably with regard to their possible use as metal-piercing projectiles. In 1886 Brustlein published

an Iron and Steel Institute paper entitled "On Chrome Pig Iron and Steel" (4). This gives data on the manufacture and properties of chromium steel, but there is almost no reference to the use of such steel for tools.

The work of the French manufacturers of chromium steel was mentioned by H. M. Howe in his book on "The Metallurgy of Steel," which appeared in 1890 (5). Howe refers to the great interest in the chromium steels as evidenced by the exhibits at Paris. In one table he gives data on the "Physical Properties of Chrome-Steel and Tungsto-Chrome Steel—Holtzer and others" (5). Unfortunately the composition of these "Tungsto-Chrome" steels is not stated. They were probably not highly alloyed, as we have no evidence that large percentages of chromium and tungsten were being used in combination at this time. In regard to the use of chromium steel as a tool steel, a single reference appears. "Holtzer also shows chromium steel which he claims will drill through Mushet's tungsten steel" (5). Although the evidence here is very fragmentary, we can clearly distinguish the trend of events in this metallurgical world. For a special tool steel, manganese-tungsten steel was in use and not at all uncommon. Plain tungsten steels were also being made and were used for various purposes. Simultaneously the chromium steels began to come into favor chiefly in the field of projectiles and armor plate; then finally came "the crossing of the alloys" as Howe calls it (6), to make the quaternary alloy steel, chromium-tungsten.

Great credit is due the French metallurgists, especially Brustlein, for their work in this field. We must also give especial recognition to the work of H. M. Howe, who by his comments, discussions and suggestions without doubt contributed greatly to the advances which were made. As an instance of the influence of Howe, attention is called to a paper by F. Lynwood Garrison on "New Alloys and Their Engineering Applications," which appeared in the Journal of the Franklin Institute in 1891 (7). This paper, incidentally, was abstracted at length in the Journal of the Iron and Steel Institute and so received notice in England and probably on the continent. Garrison quoted at length from the writings of Howe.

We know that Howe's book was circulated to some extent in England because Hadfield commented on it in 1892 (8), and praised the author for his valuable résumé of facts on chromium steel. Several pages of the book are of especial interest to us. Table 32 on page 76, for instance, gives a list of chromium steels, showing the

chemical composition of a number of samples from various sources. Two of these, No. 9 and 12, contained both chromium and tungsten. The analyses, which were furnished by Hunt and Clapp, are as follows:

No.	Carbon	Manganese	Silicon	Chromium	Tungsten
9	0.90	1.89	0.03	0.38	0.98
12	1.32	0.15	0.15	0.29	0.73

These two samples were "Brooklyn Steels," evidently having been made at the Brooklyn Chrome Steel Works. No. 12 with its low manganese is one of the earliest steels of the true chromium-tungsten type of which we have any published record.

Howe's book, or parts of it, were published serially in the "Engineering and Mining Journal," prior to the publication in book form. The list of chromium steels designated as "Table 32" was published in 1887 (9).

Another early reference to chromium-tungsten steels is found in the paper of B. F. Hart and J. Calisch of the Stevens Institute of Technology published in 1889. This paper is entitled "Chrome Steel," and gives a description of the method of manufacturing this steel at the Brooklyn Chrome Steel Works (10). An abstract of the paper which appeared in 1889 in the Journal of the Iron and Steel Institute of Great Britian, included a table giving the composition of two "Magnet Steels." The analyses as recorded are as follows:

No.	Carbon	Chromium	Tungsten	Manganese
1	0.957	0.494	0.618	0.017
2	0.965	0.597	0.761	0.017

Although the percentages of chromium and tungsten here are comparatively low, it is nevertheless of considerable interest to find such an early record of genuine chromium-tungsten steels.

Thus we see that at least a few chromium-tungsten steels had been made in the United States prior to 1890, but no doubt the development in this direction was extremely limited. It is difficult to find any evidence that such steels were being made for use as tool steels. As a matter of fact the chromium-tungsten tool steels made by the Midvale Steel Co., in the years 1894 to 1898, were not the successors of any early American alloy steels, but were copies of importations from France. It was Brustlein who first made the chromium-tungsten steels which were used as lathe tools and which "gave

the blue chips when cutting." This chapter in our story was told but a few years ago in the *Revue de Metallurgie* (11), so that only an outline of that history will here be reported.

In 1891 Brustlein's company, The Holtzer Steel Works, was closely allied in a business way with the Midvale Steel and Ordnance Co. In January 1893 Brustlein sent to the Midvale Co. two sample steels of the following analyses:

	Carbon	Manganese	Chromium	Tungsten
(1)	1.49	0.34	1.51	4.76
(2)	1.66	0.64	2.40	6.59

These we see are the true chromium-tungsten type. These steels evidently proved to be quite successful as tool steels, for almost immediately after this the Midvale Co. began to manufacture more steels of the same type. They were found to be superior both to plain carbon and to chromium tool steels (12, 13).

Among the steels which F. W. Taylor used in his lathe tool cutting tests of 1894 were some of these Midvale chromium-tungsten steels. Tool No. 70 for example is a "Midvale steel" of the following analysis:

Carbon	Chromium	Tungsten	Manganese	Silicon
1.143	1.830	7.723	0.18	0.246

Taylor also tested several other brands of "self-hardening steel" which were then on the market, and in his 1906 report he gave the names and compositions of the five brands which proved to be the best in 1898 (14). Only two of these five were strictly the chromium-tungsten type with low manganese. One was the "Midvale," the second was "Sanderson." A steel designated as No. 72, "Sanderson" and analyzed in 1894, according to Taylor, had the following analysis:

Carbon	Chromium	Tungsten	Manganese	Silicon
1.400	2.410	4.537	0.324	0.216

Seven steels of four different brands, including Sanderson, are listed as having been analyzed in 1893 (14). All of these were the high manganese (Mushet) type, with manganese at least 1.80 per cent. Two of them had 1.35 per cent chromium in addition to the high manganese. Judging from the available data, we must infer that the Midvale and Sanderson companies were the only ones who as

early as 1894 had taken the important step of abandoning high manganese altogether and substituting high chromium for it. It was at the Midvale Co., the first chromium-tungsten steels were obtained from Brustlein, as has already been shown. At the Sanderson Works, steels of the same type seem to have been developed independently. It has been impossible to secure any direct information on this point. In any event, steels of the true chromium-tungsten type were available to Taylor in 1894, although at that time no one realized their great potential value.

The steel makers themselves apparently did not consider these newer steels exceptionally fine products and very greatly superior to any then existing. If they had, their own development work during the next four years would have been conducted more vigorously and probably much differently.

The leading companies, it is true, were making some advances, and by 1898 were no doubt making comparisons of types and working toward a greatly improved steel. We know that the Midvale company at this time was marketing one of the best of the air-hardening steels, and we can also trace certain progress that was made at the Sanderson Works. Dr. E. L. French, one of the ablest of the crucible steel makers of the time, was very active in this field and was a leader in bringing out newer and better steels, both chromium-molybdenum and chromium-tungsten types. We have no record that any change was made in the heat treatment of any of these steels except by Taylor and White.

An interesting side-light on the question of the origin of the chromium-tungsten steels is found in the comments and claims made by British and German metallurgists in the years subsequent to 1900, after the Taylor-White demonstration at Paris. Statements were then made that chromium-tungsten steels had been manufactured and tested both in England and in Germany as early as 1894. In 1903 Sir Robert Hadfield called attention to the early work of T. Blair who had described some promising chromium-tungsten tool steels at Sheffield in 1894 (15). In the discussion which followed Hadfield's paper, Joseph Bedford gave additional information with regard to these steels, but unfortunately did not state their chemical composition (16).* We know now that Blair indeed must have been very close to the discovery of the usefulness of the chromium-

*In U. S. Patent No. 535,659, applied for in 1894, Bedford specified 1.50-1.90 carbon, 3.0-3.5 chromium, 0.5-1.5 manganese, and 3.0-3.5 tungsten.

tungsten steels. As evidence of this we have his brief discussion of an earlier paper by Hadfield, (8) "Alloys of Iron and Chromium," where he states his opinion that an excellent self-hardening tool steel could be produced by using both tungsten and chromium (17). Blair, however, failed to develop his ideas to the point of discovering the remarkable properties of such steels with high heat treatment.

In 1901, F. Heissig, who was a representative of Böhler Bros. & Co., a leading German firm, stated that at about the time of the Taylor-White discovery they too had been experimenting in the same direction (18). Another German writer, C. Caspar, also reported in 1901 that he had made an excellent tool steel in 1895, which "differed altogether from Mushet Steel, and was much more workable" (19). Although the exact composition of these steels is not recorded, it is probable that they were chromium-tungsten steels.

The composition of one of these German steels called "Naturharter Chrom-stahl" is given by Thallner (34), as follows:

Carbon	Manganese	Silicon	Chromium	Tungsten
2.32	0.95	0.75	6.3	0.63

This steel was introduced by the Bismarckhütte, prior to 1900. With its high chromium and low tungsten, it differs considerably from the Midvale type.

There is little doubt that such steels existed in 1895 and that a gradual improvement in tool steels was being carried forward in several of the world steel centers, but no really sensational advances occurred until Taylor and White made their great discovery at the Bethlehem Steel Company late in October, 1898.

Since this very interesting story has been told and retold many times, it will not be repeated here, but a few general comments on the work of Taylor and White will be made.

Almost twenty-five years have now passed since the patent case decision was made, and it is now easier than formerly to write dispassionately and to make a fair estimate of their achievement. They have been highly praised as great inventors; their work has been called "epoch-making" and "revolutionary." On the other hand they were at one time bitterly attacked, and their knowledge of metallurgy was ridiculed. They were denied valid patents by the court, and by inference, some have supposed that they did not actually invent anything. Insinuations were made that they succeeded as much

as they did only because they were good advertisers and because their business associates were more powerful than competitors; also that they stumbled upon the high heat treatment by accident, and that they were lucky discoverers. At present their reputation seems to be secure and they probably need no further defense; at the same time, every additional estimate of their work has a certain value, especially when it is a carefully considered judgment.

The praise of Taylor and White has certainly been a little extravagant at times; it is proper to discount to some extent the unqualified praise, but even so the final judgment is not greatly altered. It is impossible to evade the fact that Taylor and White accomplished and demonstrated what others had missed. Thus they made a tremendous contribution. It is true they did not invent a new steel. What they actually did was to demonstrate the potentialities of the chromium-tungsten type of tool steel. One writer in a rather recent review of their work has said, "The one thing that Taylor and White really discovered . . . was that a much higher hardening temperature was required for high speed steel tools than for ordinary carbon steels" (20). This we believe to be an understatement, because another very important thing they discovered was that such a high hardening treatment was much more beneficial when applied to a chromium-tungsten steel than when used for a Mushet steel. It is noteworthy that in the original patent application the recommended heat treatment is proposed for a chromium-tungsten steel and not for a manganese-tungsten steel. A chief result of their work proved to be the abandonment of the old Mushet type steel. Taylor and White were not the parents of the baby chromium-tungsten steel, but they certainly gave it its big start in life.

With regard to the question of how they came to make this great discovery while other experts in the field missed it, perhaps the best answer is to be found in the character of Fred W. Taylor. Maunsel White, as a well-trained metallurgist, no doubt contributed his share of ideas, (and this was recognized by Taylor) but as Copley says, Taylor was "the instigator, the driving force" (21). His attainments are a sufficient testimony to his unusual engineering ability, and one of his chief hobbies, as everybody knows, was the cutting of metals. This led him to make an intensive study of tool steels. If space permitted, many examples could be given to show his use of planned experiments, his devotion to the scientific method, his avoidance of fallacious reasoning. Although his statements as

to the amount of time spent on the metal-cutting investigation (35) are somewhat exaggerated, it cannot be disputed that for many months he gave practically all of his time and attention to this one problem. Probably no one will deny his industriousness. Taylor states that he personally hardened hundreds of tools (36), and during the winter of 1894-5 he spent many days running the lathe (37). In view of all this, the story at one time in circulation that Taylor and White were "lucky" does not bear close inspection. In one respect and one only were they lucky, that the steels selected by them for test included a type with great possibilities, and one so new it had not been thoroughly tested.

The precise contribution of Maunsel White is a point not firmly established. The chronological record shows that White joined Taylor in the tool steel investigation on October 23, 1898, and that it was only eight days later that the real discovery was made. White's knowledge of steels and heat treatment probably supplemented Taylor's preliminary work in a very effective way. White may have understood better than Taylor the relation of the composition of the steel to the heat treatment, although this is uncertain. A statement by White (38) seems to indicate that he was especially interested in the effect of the chromium content on the efficiency of the steel after the high heat treatment, and this, as we now know, was a very important point. He also refers to the invention of the low heat treatment.* Taylor's willingness to share with White in the profits of the invention is good evidence that White must have made some definite contribution. No doubt he aided greatly in the development work in 1899 and 1900, when the systematic attempts to find the best composition were being made and the heat treatment was being perfected.

In the tool steel world, the period from 1900-1906 has been aptly described as one of "feverish activity" (39). The unexpected and astonishing announcement that Taylor and White had invented a new process for treating tool steel and were demonstrating phenomenal results with cutting tools was sufficient to start hastily renewed experimental work in the mills of the tool steel manufacturers. It was inevitable that rapid progress should then be made, and it is not surprising that many improvements were soon made in the composition of the steel. In 1900 Taylor and White were recom-

*See page 790.

mending a steel with 1.85 per cent carbon, 3.80 per cent chromium and 8.00 per cent tungsten. By 1903 they had changed over to the so-called "low-carbon, high-tungsten" type with about 0.70 per cent carbon and with at least 14 per cent tungsten. By 1906 Taylor had approved still further modifications and was able to recommend an analysis which came close to being a standard for a good many years.

We are indebted to Dr. J. A. Mathews for some interesting historical notes on the "evolution" of the high speed steel during this period (*22*). "It is probable," says Dr. Mathews, "that we shall never know who took the radical step and made the first low carbon, high tungsten high speed steel . . .". It is true that by 1906 Taylor had adopted this type steel and had proved its superiority to his own satisfaction, but it seems evident that he was not its inventor. In fact he later admitted that this development was the work of others, but claimed that certain statements in the Taylor-White patent "suggested the very evident line of future investigation." He further brought out the fact that lowering the carbon made possible the large increases in tungsten and chromium content without interfering with the forgeability (*23*).

The policy of secrecy with regard to compositions prevailed so generally during this period that it is hard to determine just where the first of the lower carbon steels appeared, but we know that by 1902 "the change had already taken place in America, England and Germany" (*22*). Probably the English were among the first, if not the first, to adopt the improved type. J. M. Gledhill of the firm of Armstrong, Whitworth & Co., made a report in 1904 on extensive experiments his firm had made in this connection, and stated that a carbon content between 0.40 and 0.90 was found to be best (*24*). The exact date of these experiments is not given, but it is quite probable they were made as early as 1901. Another bit of evidence that the British were quick to make the modification is found in the somewhat boastful statement of J. T. Nicolson which appeared in a British trade journal in 1901. "The Sheffield makers," he wrote, "were able in a few months to produce an article far superior to that made by their rivals" (*25*). An anonymous article in *The Engineer* for September 18, 1903, stated that the composition of the English steels about 1901 was carbon 1.20 per cent, tungsten 10.5 per cent, and chromium 2.75 per cent with low silicon and manganese, but that the carbon was later reduced to about 0.70 per cent (*40*). In France, also in 1904, a modified composition was

recommended. LeChatelier noted (26) that a steel with 0.50 per cent carbon, 12 per cent tungsten and 3 per cent chromium was superior to steels of the original Taylor and White composition. The net result of all the trials and tests made in the various countries was to lead to the general acceptance of the well-known high speed steel now usually called "the 18-4-1 type."

The steel called "best" by Taylor in 1906 contained about 0.30 per cent vanadium. In later years the vanadium content was increased to approximately 1 per cent. This addition of vanadium was without doubt for many years "the only general addition that has been made to the earlier types which seems to afford universal improvement in quality" (22). Dr. J. A. Mathews was a pioneer in this field, and although Gledhill, Taylor and others also made experiments with this alloy, it was Mathews who obtained the first patent for improving high speed steel by the addition of vanadium. This was issued on January 3, 1905.

The Taylor-White discovery was made late in the fall of 1898. From this time up until 1903, the published record of many of the events is very incomplete. In general the activities of the tool steel companies were kept secret, and certain details which we would like to know cannot be ascertained, but we do have reliable information as to some of the principal events.

At the Bethlehem Steel Co., in 1898, there was no doubt at all that Taylor and White had made a great discovery. It was recognized as such by officials of the company, patents were applied for and issued, and later, after some negotiation, the two men sold their patent rights to the company. Copley is authority for the statement that each of them received almost $65,000 from the company.

After considerable further experimental work in 1899, Taylor was placed in charge of the selling of the rights or licenses to use the new process. This was in 1900 and the early part of 1901. The "shop rights" were sold to the Link-Belt Engineering Co., and several other firms with very little delay. The English rights were sold to Vickers' Sons and Maxim for $100,000.

Meanwhile, a number of demonstrations of the new cutting tools had been made at various places. (See Chronological Table, appended.) In these tests made in 1900 the so-called Taylor-White tools were easily proven superior to other brands of tool steel then on the market. As the result of the Franklin Institute Committee Test, made late in 1901, Taylor and White were awarded the Elliott-

Cresson Medal of the Institute. Charles Day was chairman of the committee which made the investigation. Tests were made at the Bethlehem Steel Co., using a number of brands of air-hardening steels treated in accordance with the manufacturers' instructions. Brands included were Mushet, Sanderson, Boreas, Raeburn, and Benj. Atha. None of these gave results as good as the tools specially treated by Taylor and White (*27*).

At the time of the earliest of these demonstrations the makers of the competing steels must have been greatly chagrinned, but as we know, they were not defeated. By 1902 several manufacturers claimed to have tools giving results "quite equal to the Taylor-White" (*27*). Further developments came rapidly. Newer and better high speed steels appeared so frequently that users of tools had difficulty in keeping up with the advances made (*28*). By 1903 some of the competing manufacturers had indeed not only equalled, but had surpassed the original Taylor-White tools.

Now followed a great controversy as to how they had done it. Taylor naturally enough believed that they had "stolen" his and White's invention (*29*). The tool steel makers, also naturally enough, denied this. The probabilities are that they obtained their superior results not only by using high heat treatments such as were recommended by Taylor and White, but also by modifying the composition of their steels. The whole situation was therefore complicated. To a side-line observer who is trying to be impartial, it does seem quite evident that the really important part of the Taylor-White process was appropriated and used without compensation to the inventors. To be sure, certain legal questions were involved such as whether what was discovered was patentable, and whether the patent claims were properly worded, etc. These points had to be, and finally were, decided in the courts.

By reviewing this development from the metallurgist's point of view, we get a clearer insight into just what happened. In 1898 the true chromium-tungsten steels were comparatively new, in fact, they were in the development stage. Taylor and White made a study of these steels and compared them with the older Mushet steels but they avoided certain errors which others made. It seems to have been a common assumption that all self-hardening steels would require similar heat treatment for optimum results. To be specific, the reasoning in 1898 was as follows: Mushet steel is better if not overheated; therefore all air-hardening steels are better if not over-

heated. Taylor and White, however, made the observation that the Mushet steels were red-short at the higher heats, while the Midvale steels were not, and they took advantage of this observation. The further investigation of this difference in behavior ultimately led to the crucial tests of October 31. They also showed that treated tools with very coarse shiny fractures were nevertheless superior tools. This was also probably at variance with commonly accepted ideas. Taylor and White were inventors because they were the first to disclose that extremely high heats were beneficial for chromium-tungsten steels. After this idea had once been disclosed, all tool steel makers of long experience were in a position to go ahead and make great advances.

The English could do this, as we have seen. Similar developments also took place in Germany. In this connection the story of the Thallner trip to Bethlehem is illuminating. O. Thallner was a German engineer and steel expert associated with the "Bismarckhütte", makers of tool steel. Following the impressive demonstration at Paris in 1900, his firm had obtained an option to purchase the Taylor-White process, and Thallner therefore made a visit to the Bethlehem Steel Co. plant to obtain more information. His final report was unfavorable and his firm did not purchase the rights. Several objections to the steel and the process as used at Bethlehem are listed in his report (30). Without going into these in detail, it is sufficient to say that they were probably valid objections. A most significant statement made by Thallner was that he believed it would be possible to produce a steel having all the good qualities of the Bethlehem steel, and not its bad ones. The incident thus brings out quite clearly two facts: First, that the new steels were not fully developed when patented, and second, that the Germans with the Taylor-White ideas as a starting point, rightly believed they would find it easy to produce a first-class "quick-cutting" steel.

In order to make our record as complete and impartial as possible, we now turn to certain unfavorable comments on the work of Taylor and White. A study of Taylor's own account of the development together with other existing evidence compels us to acknowledge that he and White did not give sufficient credit to other metallurgists and steel makers who made important contributions. The facts are these, to state them bluntly: Taylor and White did not invent the steels they used in their experiments, but used and copied steels made by others. Taylor admitted this in 1906 (41), making

it quite clear at that time, but earlier, that is in 1900 and 1901, this was not understood by the general public. Many people thought an entirely new steel had been invented or "developed." Camp and Francis state that in 1900 "the information was given out that the steel had been developed by Fred W. Taylor and Maunsel White, both employees of the company, and for some two years or more the steel was known as Taylor and White steel" (42). Hoyt says that "this steel, after suitable heat treatment, was regarded as a new metallurgical product" (43). Even in 1906 Taylor referred to the "original Taylor-White" steel, and to "the time when modern high speed tools were invented by Mr. White and the writer" (44). At this time he was usually careful to refer to "tools, as developed by us," and not to "steel."

It would not be fair to intimate that Taylor and White were personally guilty of misrepresentation. The worst that can be said is that they knew that many people had the wrong impression as to the precise nature of the invention, and they did not take the trouble to set them right; but their position as employees of the Bethlehem Steel Co., and their obligations to the company made it impossible for them to make any statements except such as might be approved by the company. The Bethlehem policy was to withhold exact information as to the chemical composition and heat treatment of the steel, and to sell licenses for the use of the process. In the early paragraphs of his 1906 report, Taylor himself mentions the secrecy that was employed for many years and gives his reason for it (the financing of further experiments). He was justifiably proud that all concerned had proven their integrity. Interesting evidence regarding the great secrecy in May, 1900, is shown by the contract of the Link-Belt Engineering Co., signed when they purchased their shop rights (45). They agreed to keep the process secret, especially the chemical composition of the tool steel, and not to sell, loan or give away any treated tools, or permit any of these treated tools to be taken outside of their shop. Such secrecy as this of course prevented the inventors from giving out any exact information as to the nature of the invention.

By 1906, however, the conditions had changed so much that secrecy was no longer necessary. Taylor may therefore be criticised with some justice because he did not then sufficiently acknowledge his real indebtedness to other workers. Although he listed the names of the steels he used, he did not give as much credit to the Midvale

Co., and to the Sanderson metallurgists as they deserved. He was also inclined to claim a little too much as the invention of himself and his associates, when actually some of the developments were the work of others. On the other hand, he was far ahead of most of his contemporaries in some respects, and he is entitled to great credit for publishing such complete data in 1906 at a time when publications of that sort were very rare. As everybody knows, his report was an exceptionally valuable contribution to the advancement of the art.

There is no disputing that the steel compositions recommended by Taylor and White in their patent applications of 1899 and 1900 were not nearly as good as those proposed only about two years later. The invention was only partially developed when the patents were applied for and great improvements were made by others, as has already been stated. It is quite generally known that the "original Taylor-White steel" was much too high in carbon. In their experiments Taylor and White had used one steel with 1.14 per cent carbon and another with 0.86 per cent carbon, yet they recommended 1.85 per cent carbon. Taylor later practically admitted that this was a mistake, and gave an explanation for their adoption of the higher carbon (46). He also claimed, as stated before, that they had suggested the possibility of using the lower carbon, which of course cannot be denied. Incidentally, the use of the very low carbon with any considerable amount of alloy was a practical impossibility in the early days as has more than once been pointed out (22), because of the fact that low carbon ferro-alloys were not obtainable prior to 1900.

It has also been asserted that the increase in cutting speed made possible by the modification of the Taylor-White composition was very much greater than the increase shown by the original Taylor-White steel in comparison with the Mushet steel (47). Regardless of whether or not this is strictly true, Taylor and White are justly given credit for having led the way. As Gledhill stated in 1904, they "initiated high speed cutting," (24) and it is still true, as remarked editorially in the *Mechanical Engineer* of Manchester in 1900 (48), that they deserve credit "for having first shown the extent to which the cutting speeds of metals with specially prepared steel tools can be pushed."

Many of the early Taylor-White tools must have been seriously defective, or to say the least, very unsatisfactory. Reference has al-

ready been made to Thallner's objections. In substance he stated that the steels had a narrow heating range, the required heat treatment was carried out only with difficulty, the tools were easily cracked, and they could not be used for cutting very hard metal (30). Taylor himself noted that the early steels were "exceedingly sensitive" to overheating on the grindstone, were not a success when using fine feeds, and lacked uniformity (49). The first steel recommended in 1899 was evidently not satisfactory for machining the harder materials, so that a second composition was later recommended for this purpose in the second patent application dated August 10, 1900. The first steel, incidentally, was a Midvale type with 2 per cent chromium and 8 per cent tungsten, while the second was a Sanderson type with 3.80 per cent chromium and 8 per cent tungsten. Sanderson probably first introduced this steel with approximately 4 per cent chromium, which later was copied by Taylor and White (50). Rushmer in 1903 stated that the early tools crumbled at the cutting edges, especially when cutting hard tough materials, and that they were very quickly superseded by a "superior steel." He probably meant the type with lower carbon and higher tungsten, although he did not give out the composition (51).

A further commonly made criticism of the Taylor-White process was that the recommended heat treatment as disclosed in the patent application was much more complicated than necessary. Competing firms were quick to make capital out of this, emphasizing that only a simple heat treatment was required for their own steels. The Taylor-White heat treatment, it is true, was described in such a way as to make it appear complicated, but actually it consisted only of a quench from a high heat into molten lead, followed by a reheating. This is now quite universally approved except that the quenching into the lead bath is considered unnecessary by many.

Another charge which Taylor and White had to face was that all they did was to take a modification of Mushet steel, and use a slightly different heat treatment for it. We have already sufficiently discussed the changes in composition. As regards the heat treatment, even F. M. Osborn, who was the most active in this phase of the controversy, conceded that Taylor and White had "further improved" on the Mushet treatment (52), and Nicolson (53), writing for an English journal in 1903, stated that Taylor and White had used "much higher temperatures than had ever before been tried." Other interesting comments are the following: Daniel Adamson

stated that "in using Mushet steel the old instructions were that the metal was not to be overheated"(54), and H. N. Bickerton said that "it was quite understood that the steel which Mr. Osborn's firm made five or six years ago would not compare with the high speed steel" (54). Note that these last two statements were also made in England in 1903.

One of the most puzzling of all the questions connected with this tool steel development is with regard to "the breaking-down point" theory of Taylor and White. It is difficult to determine to what extent this theory was correct. During the patent litigation it was severely criticised. Judge Cross in his formal opinion (69) stated that it was not substantiated by the tests made during the course of the trial. Taylor and White claimed that a tool heated to temperatures between 1550 and 1700 degrees Fahr. was inferior to tools heated in the range of 1500 to 1550 degrees Fahr., as well as to tools heated in the high range above 1725 degrees Fahr. In other words there was a "breaking-down point" for air-hardening steel somewhere between 1550 and 1700 degrees Fahr. There is little doubt that Taylor himself was firmly convinced that this was true; in his 1906 report he was positive in his statement that the tools were seriously injured if heated to temperatures within this range (55). He was then referring to his experiences with tools of the Midvale type, that is, to tools whose approximate average composition was 1.30 per cent carbon, 1.70 per cent chromium, and 8.30 per cent tungsten. The steel used in repeating the tests during the trial was presumably an air-hardening steel of a similar type, although I have been unable to find any report as to the exact composition of the steel then used.

It is incredible that Taylor and White should have invented a theory which had no basis in facts. It is certainly more probable that they advanced it with full confidence that it accorded with certain observed peculiarities of their chromium-tungsten tools. It may have been offered because it served to explain all previous failures to discover the beneficial effects of extremely high heats. Overheating had always been regarded as something to be carefully avoided, but now they were recommending an extreme overheating. This seemed to require an explanation, hence the theory. They agreed that a certain degree of overheating was indeed injurious; there was a certain range of temperatures which caused "deterioration," but once this range was exceeded the cutting speed of the

steel was again improved. Their own experience with the Midvale tools had taught them that sometimes these tools were surprisingly poor. The theory helped to explain that also; there must be a "danger point" somewhere. In short, the "breaking-down point" theory was seemingly very satisfactory at the time of the patent application, yet it could not withstand the attacks that were made upon it later. We must infer that it was actually defective in some respect, or that its supporters made some serious mistake in defending it.

In 1903, the Niles-Bement-Pond Co. was sued by the Bethlehem Steel Co., for infringement of the patent. Not until 1908 was the case finally settled. As everybody knows, the patents were held not valid. In commenting on his decision the judge said, in substance, that the patentees did not surpass others through novelty of procedure, but by means of special facilities, apparatus, and methods not embraced in the patents (69). Whether or not we agree with the judge is now not practically important. The case was legally settled and all steel treaters throughout the world were at liberty to make free use of the high heat process.

Even before the time of the settlement of this case, Taylor had decided to publish his data. By 1906 the more enterprising manufacturers had already secured the most essential information from the patent disclosures and through their own efforts, and there was no good reason why he should not publish. On the other hand there were reasons for believing that the publication at this time would be advantageous to him. He therefore spent several months in collecting and rearranging the data and presented his report at the American Society for Mechanical Engineers meeting in New York on December 4, 1906. At this time, Taylor was president of the American Society for Mechanical Engineers and the paper was given as his presidential address.

Its publication is counted an event of great importance because it resulted in the circulation not only of valuable data on the principles of metal cutting, but also of much reliable information regarding the newer tool steels. As E. R. Norris has said, "This paper created a profound and world-wide interest in steel" (56). At present its value to the metallurgist and user of steel has of course diminished to some extent, but its value to the student and historian is as great as ever. It is without doubt the greatest single source of historical information on the subject of high speed steel. A careful study of this report and a linking of its revelations with certain in-

formation from other sources enables us to answer with considerable assurance the much-debated question as to just what Taylor and White invented.

In order to produce a metal-cutting tool of high efficiency, they specified a method of heat treatment and applied it to a known type of steel so as to give it the previously unknown property of red-hardness. The proposed heat treatment combined several steps and this combination was original and novel. They were probably the first to introduce a hardening treatment separate from the forging, when treating air-hardening steels. Prior to 1898 the only heat treatment used for such a steel was the forging and the cooling from the forging heat. There was then no separate hardening operation, as we know it. This fact is apt to be overlooked by steel treaters of the present day who are accustomed to thinking of forging and hardening as separate and distinct operations. In the method of Taylor and White the heating almost to the melting point to forging. This particular step is so important that it is generally regarded as their chief discovery.

Another part of the process was the use of the second or low heat treatment, or the "high draw" as it is usually called today. This is considered by some to be a greater and more original invention than the use of the high heat. Although today the great value of such a step is almost universally recognized and the reasons for its value are well understood, it is an interesting fact that a good many years passed before it was so widely approved. With regard to its origin, we quote the statement of Maunsel White, made in 1904. "After the high heat it was found that the tool made further improvement by running in the lathe and grinding several times. This we found was due to the heating in cutting and for this was substituted a second heating at a low heat which was carefully determined by exhaustive experiments to obtain maximum results" (38). This clearly shows how the high draw came to be invented. A controlled reheating was adopted as an important step in the process. Taylor also refers to this subject in paragraph 995 of his 1906 report, but his statement is not quite as definite as White's. We note that the treatment recommended was a rather brief tempering (5 minutes at 1150 degrees Fahr.).

Another contribution made by Taylor and White, and one frequently mentioned, was their demonstration of exceptionally high cutting speeds. Strictly speaking, this was not an invention but rather the result of the invention. Occasionally the criticism has

been made that these tests were simply "spectacular". The rapid cutting when the nose of the tool was visibly red-hot was sometimes classed as an advertising stunt. It is true this was "advertising", but the demonstrations were based on actual results obtainable by practical methods of heat treatment. Taylor and White, or some of their associates at Bethlehem, were good advertisers. The demonstrations were intended to arouse great interest in the new process and they accomplished their purpose. The interest so aroused led to widespread technical advances throughout the industrial world.

The developments since 1906 will be only briefly summarized. The steel most highly recommended by Taylor at that time proved to be a standard for many years, as has already been said. The chromium content of from 5 to 6 per cent, however, was generally reduced to 3.5 to 4 per cent in the later years, and the vanadium content was increased, so that in the United States in the years 1920 to 1930 a vanadium content of 0.75 to 1.00 per cent was probably most commonly found.

Innumerable variations have, of course, been tried during the past twenty-five years. The proportions of the elements have been varied, and additions of other elements have been made, but up to the present, no new steel has been good enough to supersede the 18-4-1 type, except as a special purpose steel.

The variations which are at the present time commercially available are principally the

14-4-2 type
15-4-1 type
20-4.5-1.5 type
Various cobalt (Supersteel) type
Molybdenum-tungsten type

In the early days of cobalt high speed steels the usual practice was to add from 3 to 5 per cent cobalt. This was later increased to 7 per cent, the recent tendency being to use higher percentages. To discuss this development adequately would require a separate paper. To summarize very briefly, we may say that such steels do appear to have a certain limited field of usefulness and in this field they are probably superior to the 18-4-1 type, but they are also considerably more expensive.

Another experimental development of interest has been the work of Keen (70), Kinzel and Burgess (31), and Oertel and Eilender (71), on the high carbon, high vanadium steels. The vanadium content in these steels is increased to as much as 6 per cent, and the carbon content is also increased. Such steels are so new that they have

Table I

Composition of Mushet Steel

		Ref. No.	C	Mn	W	Cr	Si	Date
1.	Forbes	(57)		1.73	8.73			1872
2.	Forbes			2.53	8.78			1872
3.	Gruner	(58)	1.40		7.98		0.24	1873
4.	Howe	(59)	1.24	1.04	9.99		0.33	1887
5.	Howe		1.99	0.19*	7.81		0.09	1887
6.	Ledebur	(60)	1.70	1.26	8.25		0.82 (a)	
7.	Addy	(61)	1.67	2.56	4.65		0.25 (b)	1890
8.	Nau	(62)		1.73	8.3			1892
9.	Lau	(63)	2.29	1.87	5.63	0.53	0.50 (c)	1900
10.	Hadfield	(15)	2.30	2.57	6.12		1.05	1903
11.	Hadfield		2.00	1.72	8.22		1.60	1903
12.	Hadfield		1.65	2.12	5.80	0.45	1.36	1903
13.	Reiser	(64	2.0	2.5	5.0	0.5	1.3	1903
14.	"Engineer"	(40)	1.46		9.25			1903
15.	"Engineer"		2.33	2.33	6.30	0.30	0.88	1903
16.	"Engineer"		1.99	1.90	7.81		0.09	1903
17.	"Engineer"		2.00	2.50	5.00	0.50	1.30	1903
18.	Thallner	(34)	1.8	1.7	10.5	0.5	0.9 (d)	1906
19.	Taylor	(14)	2.15	1.58	5.44	0.40	1.04	1907
20.	Taylor		2.40	1.90	5.62	0.49	0.71	1907
21.	Armstrong	(65)	1.93	2.25	9.00		0.40	1913
22.	d'Arcambal	(66)	2.38	1.73	4.80	1.12	1.15	1921
23.	Stoughton	(67)	1.85	2.50	9.0			1923
24.	Camp and Francis	(68)	2.20	1.35	6.00	0.60	(c)	1925
25.	Oertel	(72)	2.0-2.4	1.7-2.5	5.-8.	0.50	0.7-1.6	1931

*Probably a misprint for 1.90.
(a) Named "English", but not "Mushet".
(b) "Ivanhoe" brand, not called "Mushet".
(c) Self-hardening, not named as "Mushet".
(d) The chromium was found in some samples, not in all.

not as yet been thoroughly tested. It is possible that they will prove to be of value, but they, like the high cobalt steels, are expensive steels to make.

Another quite recent development is the production of the molybdenum-tungsten steels. Molybdenum tool steels, as is well known, are not new, as some steels containing molybdenum were made as early as 1898. It is only within the last year, however, that the new molybdenum-tungsten steel has been announced. This is different from all previous varieties, in that it contains about one-fourth as much tungsten as molybdenum. It is a distinct type, with properties superior to other molybdenum steels, as has been shown by various tests (32). This steel is also too new to be thoroughly proven, but the present indications are that it will be a competitor of the 18-4-1 type.

Within the next few years other new steels will probably appear, and tests will continue, so that eventually we shall know whether any new steel is good enough to displace the 18-4-1 type as standard. It is clearly impossible to predict the outcome with

certainty. The trend now seems to be toward a multiplicity of steels and cutting alloys, so that possibly in the future no single steel will be able to dominate the field.

Because of space limitations the historical development of the molybdenum tool steels has been only briefly mentioned. An excellent review of the use of molybdenum in high speed steel has recently been given in the monograph, "The Alloys of Iron and Molybdenum," by J. L. Gregg (33). This includes practically everything published on the subject, although it no doubt omits certain unpublished parts of the history which would be of considerable interest if they could in some way be unearthed.

Chronological Table

November, 1891—Brustlein sent manganese-tungsten steels to Midvale.

January, 1893—Brustlein sent chromium-tungsten steels to Midvale.

Winter of 1894-95—Taylor tested various brands of tool steel at Cramps'.

May 27, 1898—Taylor started to work at Bethlehem.

October 23, 1898—White joined Taylor in the tool steel experiments.

October 31, 1898—Amazing effects of the high heat treatment discovered at Bethlehem.

October 20, 1899—U. S. patent applied for by Taylor and White.

May 8, 1900—Contract with Link-Belt signed.

July 31, 1900—Demonstration at Bethlehem Steel Co., to technical press.

Summer of 1900—Demonstration of tools treated by Taylor-White process at the Paris Exposition.

August 10, 1900—A second U. S. patent applied for by Taylor and White.

September 7, 1900—Earliest printed report of Taylor-White tests at Paris appeared in England, a brief anonymous note in *The Engineer*.

November 17, 1900—British patent of Taylor and White printed in England.

Up to February, 1901—Taylor had charge of the sale of shop rights.

February 19, 1901—Two U. S. patents issued to Taylor and White, No. 668,269 and 668,270.

About July 1, 1901—Taylor left employ of the Bethlehem Steel Co.

December 20-21, 1901—Tests made by the Franklin Institute Committee.

April 11, 1902—Tests reported by the Franklin Institute Committee.

1902-03—Tests made by Nicolson Committee in England.

October, 1903—Report of tests made by Professor Nicolson.

1902-03—Tests continued by Taylor and associates at William Sellers & Co.

1903—Tests continued by Taylor and associates at Link-Belt, and composition of the steel modified.

1903—Bethlehem started suit against Niles-Bement-Pond Co. for infringement of the patent.

December 31, 1903—Lodge and Shipley tests reported.

October 26, 1904—Gledhill's paper presented at Iron and Steel Institute meeting in New York.

1905—White left employ of the Bethlehem Steel Co.

Summer and Fall of 1906—Taylor and associates tested several commercial steels.

December 4, 1906—Taylor's American Society for Mechanical Engineers address given at New York.

1908—The patent suit ended.

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LOAD LOSSES IN SMALL HELICAL SPRINGS AT ELEVATED TEMPERATURES

By F. P. Zimmerli, W. P. Wood and G. D. Wilson

Abstract

This paper presents the results of an investigation of the load losses sustained by small helical springs in the stressed condition when exposed to elevated temperatures for periods of 72 hours. It was found that tests made for shorter periods of time were liable to be misleading. For each material studied there appears to be a limiting temperature below which stress and temperature are the controlling factors and above which time is the important factor. These limiting temperatures vary from 200 degrees Fahr. to 700 degrees Fahr. for ferrous alloys, the stainless steels and high speed steel showing the best results. Monel metal shows good resistance up to 400 degrees Fahr. while phosphor bronze and brass fall off rapidly above 100 degrees Fahr.

IN MANY types of service at the present time, helical springs are required to operate at temperatures considerably above atmospheric temperatures. In this connection might be mentioned valve springs in aircraft engines, clutch springs, oven-door springs, certain types of pressure relief valve springs, and many others. All such springs suffer more or less loss in loading capacity. In general, this loss increases with increasing temperature. The purpose of the present investigation was to study load losses in various commercial spring materials at elevated temperatures and to present data which might be helpful in choice of material and design of springs for service at these higher temperatures.

While a considerable amount of work has been done in connection with the behavior of metals at elevated temperatures, there is but little published data dealing with this particular phase of the subject. Pickwell[1] discusses the behavior of monel metal springs and

[1]The Nebraska Blueprint. April, 1929.

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reports that springs made from this material perform acceptably up to 450 degrees Fahr. His work was based on short-time tests which the present authors have found to be somewhat misleading. He also points out that alloy steels are superior to monel metal above 450 degrees Fahr. Troendly[2] points out the application of monel metal for springs operating at elevated temperatures, particularly where corrosive conditions are present. Several workers including the present authors[3] have made determinations of the torsional moduli of spring materials at temperatures up to 1000 degrees Fahr.

Materials Investigated

The attempt was made to study as many as possible of the metals which are used at present in the production of helical springs. Table I includes a list of these metals, together with their chemical analyses, previous thermal and mechanical treatments, bluing temperatures, and Rockwell C hardness numbers as taken when the springs were ready for testing. By the term bluing is meant a relatively low temperature anneal given to the springs after coiling in order to remove coiling strains.

Apparatus and Procedure

The general method used in this study was to observe the load losses after the springs had been heated in the stressed condition for a definite period of time at various temperatures. Some preliminary experiments indicated that in the case of each material there appeared to be a certain temperature below which stress and temperature were the predominating factors in load-carrying capacity and above which time was the most important factor. It was found that below this temperature the springs tested had ceased to take any set after 72 hours, while above this temperature they continued to exhibit set indefinitely. With this information at hand, all tests were run for periods of 72 hours, regardless of temperature.

The free height, outside diameter, and wire diameter of each spring were measured. By means of the Wahl[4] formula, the loads

[2] Inco Publication of International Nickel Company, Vol. 6, No. 3.

[3] *Proceedings*, American Society for Testing Materials, Vol. 30, Pt. II, 1930, p. 350.

[4] *Transactions*, American Society of Mechanical Engineers, Vol. 51, Pt. I, 1929, A.P.M., 51-17-185.

Table I
Composition of Metals Tested

Material	C	Mn	P	S	Per Cent Cr	W	V	Cu	Ni	Fe		Previous Treatment	Bluing Temp. °F.	Rockwell C Hardness
Tempered Carbon Steel	0.61	0.88	0.034	0.036	.....	.....	.....	.....	.....	.....	.....	Quenched and Drawn	800	40
Music wire	0.89	0.32	0.024	0.021	.....	.....	.....	.....	.....	.....	.....	Cold Drawn	500	50
Chrome Vanadium Steel	0.53	0.63	0.018	0.014	1.03	.....	0.17	.....	.....	.....	.....	Quenched and Drawn	800	46
Stainless Steel	0.30	0.32	.....	.....	12.60	.....	.....	.....	.....	.....	.....	Cold Drawn	800	34
Stainless Steel KA2	0.07	0.43	.....	.....	17.43	.....	.....	.....	8.90	.....		Cold Drawn	800	38
High Speed Steel	0.76	0.28	0.025	0.025	4.10	18.10	1.10	.....	.....	.....	Si 0.110	Quenched and Drawn	1150	58
Monel Metal	.....	2.17	.....	.....	.....	.....	.....	31.90	64.90	1.03	.....	Cold Drawn	600	..
Phosphor Bronze	.....	.....	.....	.....	.....	.....	.....	94.20	.....	Trace	Sn 5.51	Cold Drawn	400	..
Brass	.....	.....	.....	.....	.....	.....	.....	66.65	.....	Trace	Zn 32.90	Cold Drawn	500	..

required to produce given stresses were calculated. The deflections corresponding to these loads were then measured and the springs compressed in a special jig to the predetermined deflections. The jigs containing the compressed springs were then placed in a Freas

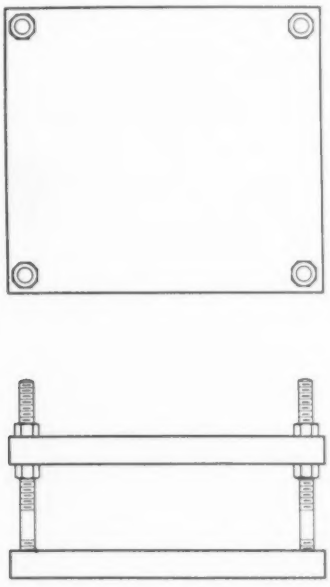


Fig. 1—Jig for Stress Tests.

oven and held at the required temperature for 72 hours, at the expiration of which time they were removed and the load losses determined. Three springs were used in each test and the results averaged.

The Wahl formula is expressed as follows:

$$S = \frac{8PD}{\pi d^3}\left(\frac{4c-1}{4c-4} + \frac{0.615}{C}\right)$$

where S = stress in pounds per square inch in outer fibers
D = mean diameter in inches
d = wire diameter in inches
P = load in pounds
$C = \frac{D}{d}$

The stress given by this formula takes into consideration shear as well as torsion and gives what is known as total shear stress.

Fig. 1 is a sketch of the jig to which reference was made above. It consists of two heavy cast iron plates, the relative positions of

which are varied by means of lock nuts. The springs were placed between these plates and the deflections obtained by proper adjustment of the lock nuts. The distance between the plates was adjusted at each corner by means of inside calipers. The plates were massive enough to prevent warping during the period of heating. No such thermal changes were observed during the period of the investigation.

Results and Discussion

Results of this study are presented in Figs. 2 to 10 inclusive, and are plotted in such a manner as to show variations in load losses versus temperature. As stated previously, these results represent

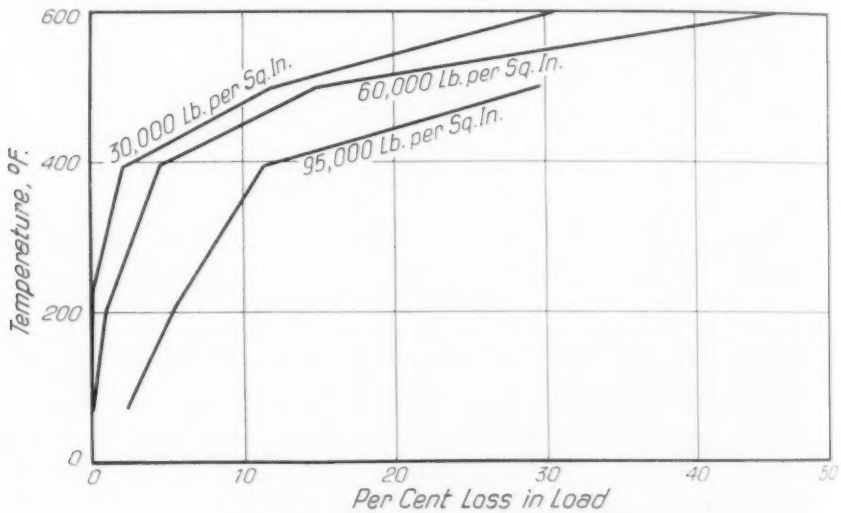


Fig. 2—Stress Tests of Tempered Carbon Steel.

values obtained after the springs were heated for 72 hours. The fact that 72 hours were required for equilibrium conditions suggests the behavior of steel in tension at elevated temperatures, in the case of which it has been noted that up to the equi-cohesive temperature, creep is observed for about 150 hours. It is postulated that the metal has become strain-hardened by this time and resists further deformation. Since results of creep in torsion, particularly with the metals used in this investigation, are rather scattered and incomplete, it is impossible to check this observation with information furnished by other investigators. This question was not thoroughly studied in the present work since the aim was primarily

to secure practical data which might be of service in the design of helical springs for use at elevated temperatures.

It will be noted that in most cases, at least two stresses have been used in determining load losses. In general, the highest stresses

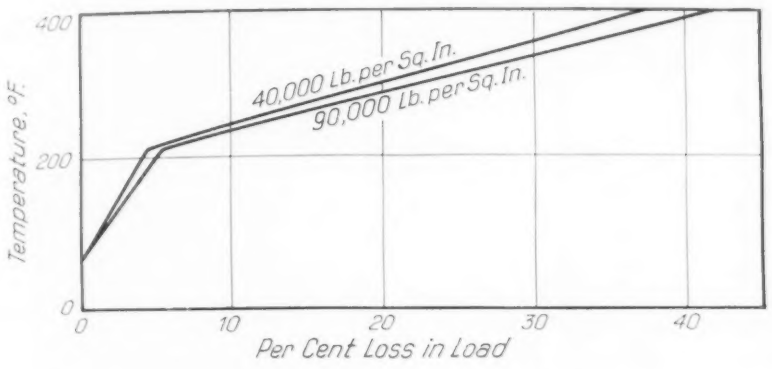


Fig. 3—Stress Tests of Music Wire.

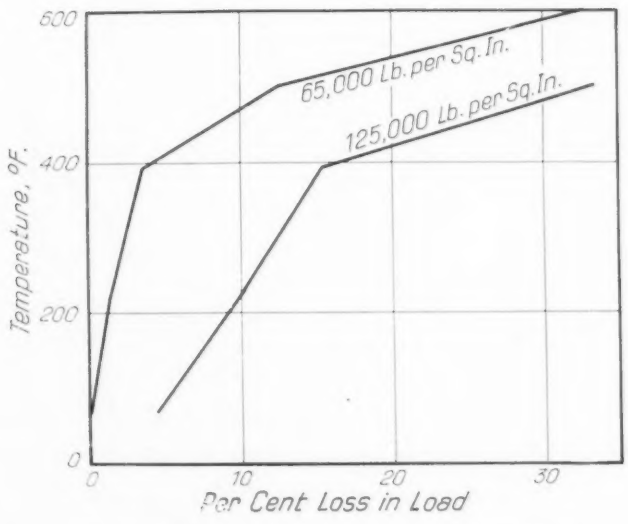


Fig. 4—Stress Tests of Chromium-Vanadium Steel.

were in the neighborhood of the maximum stresses used when springs are operating at atmospheric temperatures. The other stresses were considerably lower and were chosen as being probably in the range of lowest practical stresses which might be used in spring design.

Fig. 2 indicates that the tempered carbon steel may be used at low stresses up to 400 degrees Fahr. without load losses of more than 4 per cent. Above 400 degrees Fahr., however, in all cases a sharp increase in load losses is observed.

Fig. 3 shows the behavior of music wire which, as is well known, is a highly work-hardened material. The temperature beyond which load-carrying capacity drops off rapidly appears to be 200 degrees Fahr. An interesting point is, that in so far as this study goes, stress seems to be of relatively little importance in the case of this material. The springs stressed to 90,000 pounds per square inch

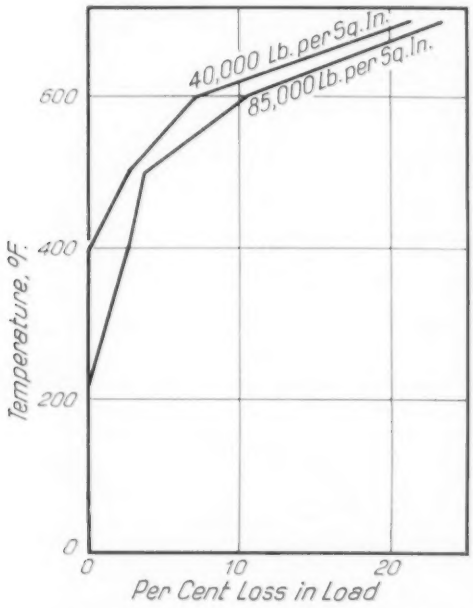


Fig. 5—Stress Tests of 12 Per Cent Chromium Stainless Steel.

show but little increase in load loss over those stressed to 40,000 pounds per square inch.

The stresses used in the chromium-vanadium steels (Fig. 4) were rather high. The fact is quite clear, however, that 400 degrees Fahr. is again the limiting temperature. Springs with stresses lower than 65,000 pounds per square inch could probably be used up to 400 degrees Fahr. with practically no loss in load and if the stresses were very low, they might be used at temperatures slightly higher than 400 degrees Fahr.

Figs. 5 and 6 indicate that the stainless steels may be used up to 500 degrees Fahr. without losses of more than about 4 per cent. There is not much difference in the behavior of the straight chromium steel as compared to KA2.

As would be expected, high speed steel (Fig. 7) may be used at temperatures appreciably higher than those for any other metal

studied. For stresses up to 40,000 pounds per square inch, this material may be used up to 700 degrees Fahr. without more than 5 per cent loss in load. Cases have been reported wherein high speed

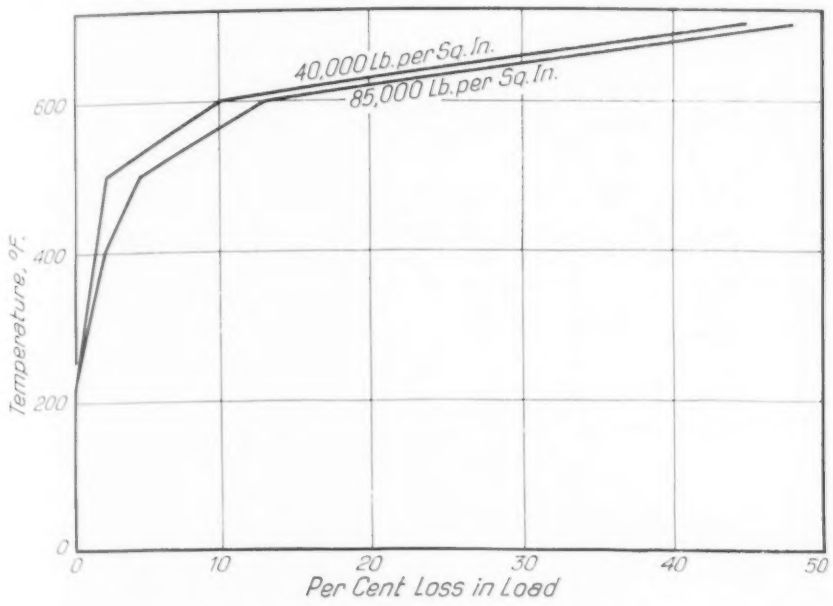


Fig. 6—Stress Tests of Stainless Steel KA2.

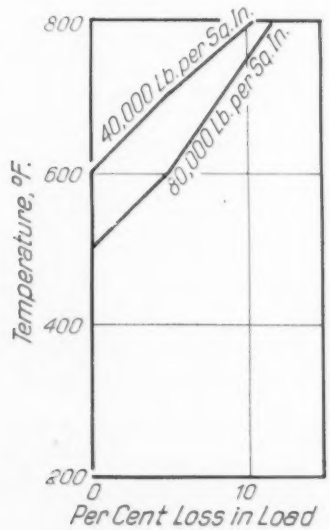


Fig. 7—Stress Tests of High Speed Steel.

steel at low stress values has given satisfactory performance at 900 degrees Fahr.

Monel metal (Fig. 8) was studied at two stresses. The higher of these was 85,000 pounds per square inch, and it is felt that this was probably somewhat above the stresses that would ordinarily be used. It will be noted that at 40,000 pounds per square inch, this

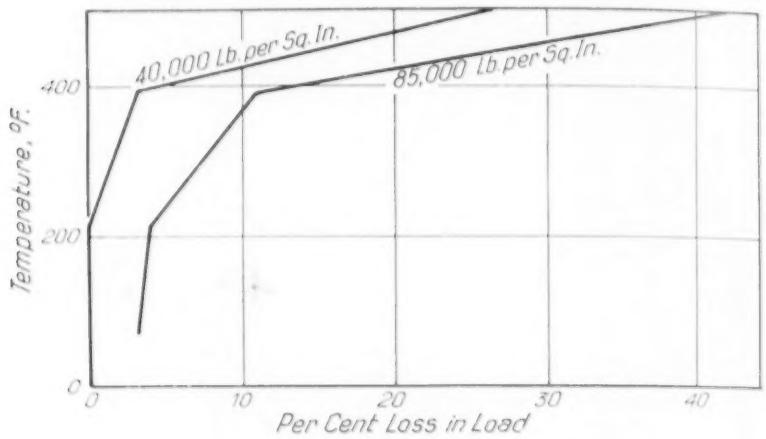


Fig. 8—Stress Tests of Monel Metal.

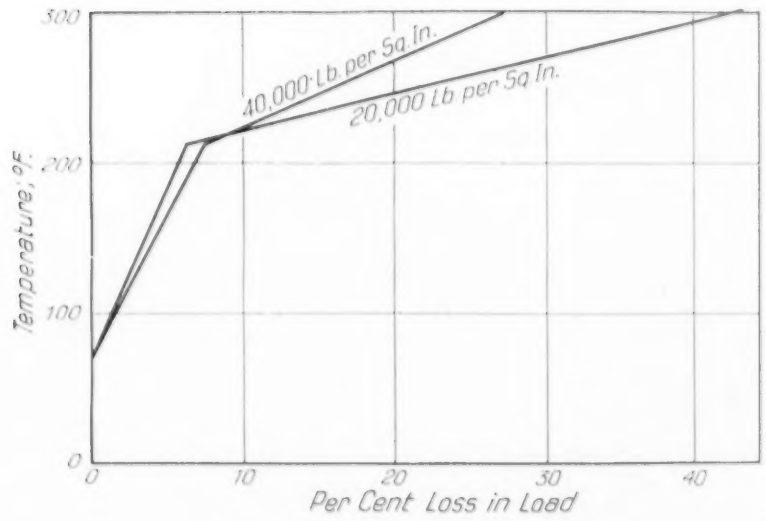


Fig. 9—Stress Tests of Phosphor Bronze.

metal gives very satisfactory performance up to 400 degrees Fahr. This fact, coupled with the well-known corrosion resistance of monel metal, would make this material very desirable in many applications.

The results for phosphor bronze and brass are presented on Figs. 9 and 10. It is evident that these materials can scarcely be recommended for any temperatures above 100 degrees Fahr. This

practically limits their use to only those applications where the temperatures do not exceed atmospheric, but where a certain amount of corrosion resistance is necessary.

Check Tests on Load Losses at Elevated Temperatures

In order to test the utility and accuracy of the curves presented in Figs. 2 to 10 inclusive, some extended checking tests were made. The procedure was as follows: Springs were subjected to specific stresses and temperatures for periods from 7 to 11 days. The load

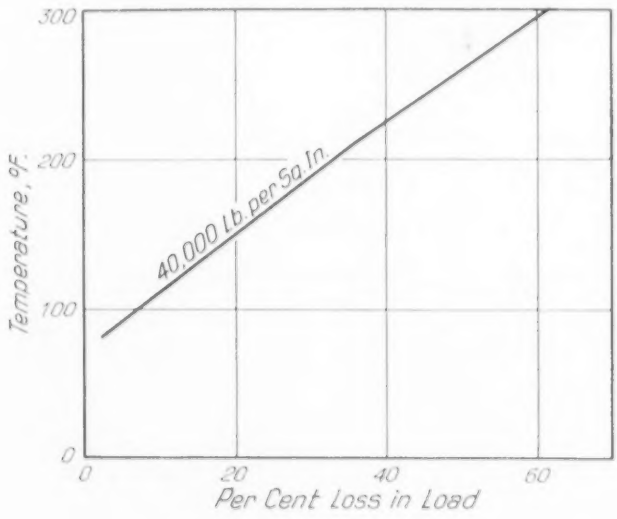


Fig. 10—Stress Tests of Brass.

losses were predicted from the curves and compared with the actual losses observed. From 2 to 5 springs were used in each test and their results averaged. Results of these tests are shown in Table II.

It is seen that the differences between actual and predicted load losses are less than 2 per cent.

Table II

Material	Temperature, Degrees Fahr.	Maximum Fiber Stress, lbs. per sq. in.	Time at Stress and Temperature	Predicted Loss in Load, Per Cent	Actual Loss in Load, Per Cent
Music Wire	212	40,000	7 days	4.8	3.5
Tempered Carbon Steel	356	80,000	7 days	6.0	4.9
Stainless Steel KA2	500	40,000	7 days	2.0	1.0
Stainless Steel KA2	500	85,000	11 days	4.7	3.0

In order to ascertain the effect of temperatures above those recommended, a group of tempered carbon steel springs were stressed to 85,000 pounds per square inch for 7 days at 500 degrees Fahr. This temperature was 100 degrees Fahr. above the limiting temperature of 400 degrees Fahr. The average load loss in these springs was 48 per cent. From Fig. 2, it had been predicted that at the end of 3 days the loss in load would be about 25 per cent. This would seem to indicate that the statement made earlier in this paper regarding the importance of time, at temperatures above those recommended, is not out of line, at least as far as these carbon steel springs are concerned.

ALLOYS OF IRON, MANGANESE AND CARBON—PART V

Microscopic Studies of Binary Iron-Manganese Alloys

By V. N. Krivobok and Cyril Wells

Abstract

The paper deals with the characteristic microstructure in a series of fairly pure iron-manganese alloys, varying in composition from 100 per cent iron to 100 per cent distilled and remelted manganese. The nature of the constituents is described and illustrated by photographs. Thus the proof is offered, augmenting the dilatometric and X-ray studies of the same alloys already published, that the iron-manganese system does not form a continuous series of solid solutions, but contains several phases, not all of which, however, have been distinguished microscopically.

IN reviewing work on the subject of iron-manganese alloys and manganese steels, one finds that, in the majority of cases at least, the alloys examined were contaminated with common impurities, such as carbon, silicon, etc. The problem of elimination of small amounts of impurities, especially carbon, is rather difficult and requires a certain tedious procedure in the preparation of alloys.[1] Yet it appears not only desirable but quite necessary to reduce impurities to a minimum if we are to expect that microscopic studies of any system will furnish reliable information. The solubility of carbon in iron at room temperature is quite small[2] (probably in the neighborhood of 0.01 per cent), and, what is more, as Dickie[2] states, additions of manganese to ferrite decrease it still further. Conse-

[1] F. M. Walters, Jr., "Alloys of Iron, Manganese and Carbon, Part I, Preparation of Alloys," Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 577.

[2] T. D. Yensen, "The Magnetic Properties of the Ternary Alloys, Iron-Silicon-Carbon," American Institute of Electrical Engineers, Vol. XLIII, 1929, p. 145.
H. A. Dickie, "The Solubility of Carbide in Ferrite," *Journal*, Iron and Steel Institute, Vol. CXX.
J. H. Whiteley, "The Solution of Carbide in Alpha Iron and Its Precipitation," *Journal*, Iron and Steel Institute, Vol. CXVI, 1927, p. 293.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Dr. V. N. Krivobok, a member of the society, is professor of metallurgy, Carnegie Institute of Technology, Pittsburgh. Cyril Wells is assistant metallurgist, Metals Research Laboratory. Manuscript received July 21, 1932.

quently, even small amounts of carbon, especially if they exceed the solubility figures, would introduce serious error in the interpretation of the structures of the iron-manganese alloys.

Possibly on account of this fact, it is commonly believed that iron and manganese form a continuous series of solid solutions which retain, at least at the iron end of the diagram, the space lattice of iron. It was necessary, therefore, to utilize for these studies alloys containing from 0 to 100 per cent manganese, with very low carbon content (between limits of 0.006 and 0.03 per cent, and other impurities practically nil. Even these alloys cannot be considered, strictly speaking, binary alloys. Yet, their study should yield much more definite information than could have been obtained from the investigation of previously available alloys of higher, although comparatively small, percentages of carbon. And, thus, it will be shown that the constituents are more numerous and, hence, microstructure of iron-manganese alloys is decidedly more complex than was previously supposed.

For purposes of description, the alloys are divided into groups based on the transformations involved rather than on the appearance of the microstructure, since the latter depends on the particular heat treatment that an alloy has received. The transformations and phases involved are best shown by the tentative diagram (Fig. 1) constructed in accordance with available information. The data given in this are from three sources: delta region and the solidus-liquidus are taken from the work of Rumelin and Fick[3] and the high manganese end from the X-ray investigations by Öhman.[4] The low manganese end is based on Walters' unpublished dilatometric observations on homogenized alloys.

It is, thus, definitely established that iron-manganese alloys may contain one or more of the following phases: alpha, gamma, and epsilon iron (on the iron side of the diagram), and gamma, beta, and alpha manganese (on the manganese side). The continuity of the gamma iron phase with the gamma manganese phase is to be noted,—that is, gamma iron merges imperceptibly into gamma manganese while the lattice dimensions are changing uniformly. Öhman has drawn a dividing line between gamma iron and gamma manganese, apparently for the sake of completeness.

[3]G. Rumelin and K. Fick, *Ferrum*, 1915, Vol. 12, p. 41.

[4]Einar Öhman, "Röntgenographische Untersuchungen über das System Eisen-Mangen," *Zeitschrift für Physikalische Chemie*, Vol. 8, 1930, p. 81.

In the first group are described those alloys which, on cooling, undergo a gamma to alpha transformation, which is complete at room temperature. Such alloys contain at room temperature only

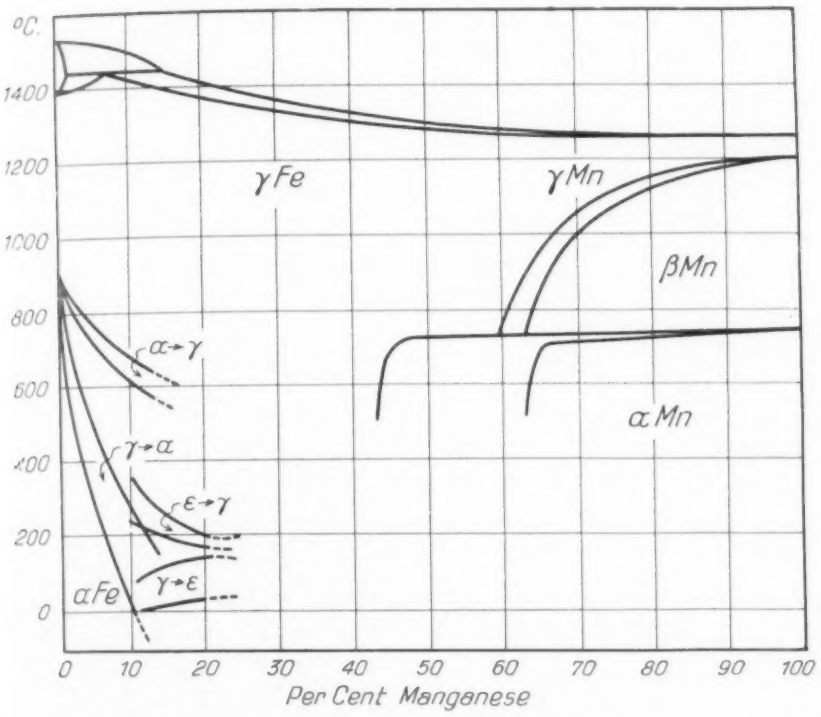


Fig. 1—Diagram Showing Regions of Various Phases in Iron-Manganese Alloys. (From the X-ray data of Öhman and unpublished findings of the Metals Research Laboratory, Carnegie Institute of Technology.)

one phase, namely, alpha iron; the composition of the alloys varies from 0 to approximately 10 per cent manganese.

In the second group are placed those alloys in which gamma decomposes to epsilon, with or without the formation of alpha.

To the third group belong the alloys (30 to 60 per cent manganese) in which all transformations are suppressed and in which high temperature gamma phase is preserved down to the temperature of liquid air. These alloys are of the simplest microscopic appearance.

From 60 to 95 per cent manganese, we have the fourth group of alloys, in which is observed, for the first time, the appearance of the manganese-rich phases, the relative amounts of which, as compared with gamma phase, depend to a large extent on composition.

Description of Various Groups of Alloys

In describing the microscopic characteristics of the alloys, the question of nomenclature is of importance. In previously published work, the alloys of iron and manganese were frequently described as "pearlitic," "sorbitic," or "martensitic," using, as it were, the descriptions borrowed from the nomenclature pertaining to iron-carbon alloys. Such a procedure is hardly justifiable. While it is true, for example, that some of the iron-manganese alloys have a microscopic appearance similar to that of coarse martensite of plain carbon steels, yet their other characteristics are so dissimilar that the application of the expression "martensite" is wholly unwarranted. For instance, the atomic structure of martensite is accepted to be tetragonal; in iron-manganese alloys no such atomic arrangement is found to exist. Moreover, the properties exhibited by martensitic carbon steels and by iron-manganese alloys showing martensite-like structure are not comparable.

Again, certain alloys, as will be shown presently, would be well described as possessing a "Widmanstatten" structure. It may be pointed out that the expression "Widmanstatten" structure, judging by metallurgical literature, implies the co-existence of at least two phases. Consulting, for example, the manuscript on crystallization of iron, by Osmond and Cartaud,[5] we read as follows: "when a body, liquid or solid, deposits successively several solid phases, the secondary or tertiary deposits lodge preferentially between certain crystallographic planes determined by the primary crystallization and thus illustrate its structure."

Dr. R. F. Mehl states more generally: " . . . . when a solid solution, stable at high temperatures, upon cooling precipitates a new phase, this new phase appears in a particular manner; it deposits in such a way that its lattice bears a definite crystallographic relation to the lattice of the parent solid solution."[6] Similar quotations, particularly in relation to meteorites, could be cited from the work of N. T. Belaiew.[7] However, studies of iron-manganese alloys (of certain composition) showing typical Widmanstatten pattern prove

[5] "Sur la Cristallization du Fer," *Revue de Metallurgie*, 1906, Vol. 3, p. 491, translated by R. F. Mehl.

[6] Studies upon Widmanstatten Structure. Part I, page 7, Technical publication No. 353. American Institute of Mining and Metallurgical Engineering, 1930.

[7] On the Genesis of Widmanstatten Structure in Meteorites and in Iron-nickel and Iron-carbon Alloys, *Mineralogical Magazine*, March, 1924, Vol. XX, 104, pp. 173-185.

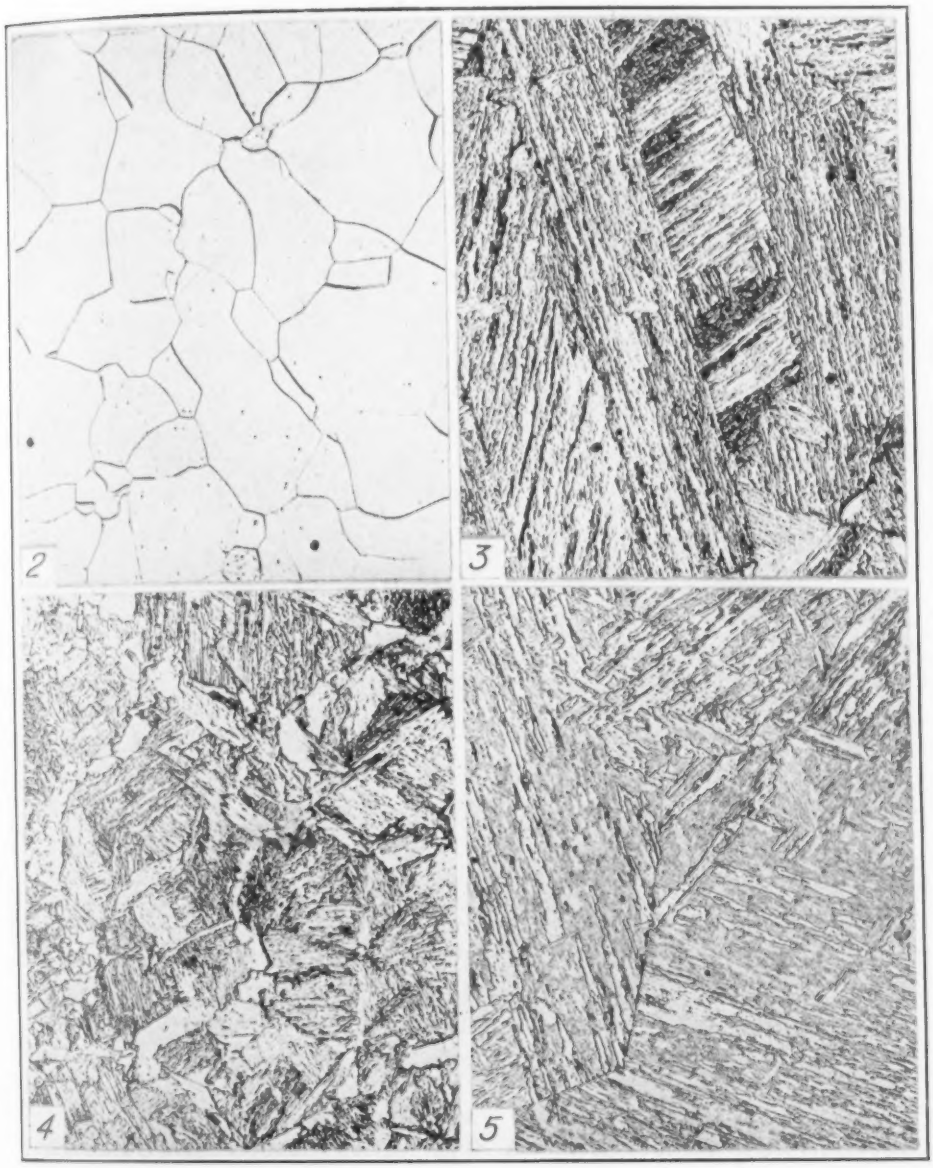


Fig. 2—Manganese 1.4 Per Cent, Carbon 0.01 Per Cent. Heated to 1200 Degrees Fahr., Held 10 Minutes, Ice Brine Quench.
Fig. 3—Manganese 1.7 Per Cent, Carbon 0.01 Per Cent. Heated to 2500 Degrees Fahr., Held 15 Minutes, Ice Brine Quench.
Fig. 4—Manganese 1.7 Per Cent, Carbon 0.01 Per Cent. Heated to 2000 Degrees Fahr., Held 30 Minutes, Ice Brine Quench.
Fig. 5—Manganese 7.2 Per Cent, Carbon 0.01 Per Cent, As-Cast. Etchant, 5 Per Cent HNO_3. All Photomicrographs × 250.

the existence of only one phase in these alloys, as shall be described presently.

Group I — The characteristic structures obtainable in this group

are adequately represented by the photomicrographs Figs. 2 to 11 inclusive.

The structures are found to fall into two distinct and definite types: one, as exemplified by Fig. 2, and the other as is shown in Fig. 3 or 4. The first is in no way different from the structure of pure metals or of homogeneous solid solutions:—definitely outlined grains of various sizes, controlled, of course, by the heat treatment. This structure is readily obtainable in the alloys of not higher than 2 per cent manganese, either in as cast condition or, preferably, very slowly cooled with the furnace. There can be no doubt that it contains but one phase.

The second observed structure, much resembling in appearance what is known in metallographic nomenclature as "Widmanstatten" and described as such by Hadfield,[8] Wohrman,[9] Ishiwara,[10] and others, is characteristic of the alloys up to 2 per cent after quenching (Figs. 3 and 4) and of the alloys higher than 2 per cent manganese even after slow cooling (Figs. 5 and 6). It must not be forgotten that despite the close resemblance to Widmanstatten pattern, which, as was previously stated, contains at least two phases, manganese-iron alloys of the similar (i. e., Widmanstatten) structure, contain mainly one phase (namely, alpha iron) as has been proven by X-ray analysis.[11]

Thus, the presence of "Widmanstatten"-like structures in iron-manganese alloys presents an interesting phenomenon. The explanation, however, suggested itself after the study of dilatometric behavior of these alloys and simple experimental work. Taking for example an alloy with 4.4 per cent manganese, it will be noted that in an "as-quenched" condition (Fig. 7) the structure inside large grains is revealed as a set of indistinct black parallel lines, running in many directions,—in other words, a typical Widmanstatten appearance. On slow cooling of the same alloy the picture is materially changed (Fig. 8)). The general appearance is more or less preserved but the structure proper is no longer characterized by

[8]Sir Robert Hadfield, "Alloys of Iron and Manganese Containing Low Carbon," *Journal*, Iron and Steel Institute, Vol. 115, 1927, p. 297.

[9]C. R. Wohrman, "Heterogeneity of Iron-Manganese Alloys," Technical Publication No. 14, American Institute of Mining and Metallurgical Engineers, 1927.

[10]Torajiro Ishiwara, "On the Equilibrium Diagram of the Al-Mn, Cu-Mn and Iron-Mn Systems," Science Reports, Tohoku Imperial University, Vol. 19, 1930, p. 999.

[11]M. Gensamer, J. F. Eckel and F. M. Walters, "Alloys of Iron and Manganese. Part III,—X-Ray Study of the Iron-Manganese Binary Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 599.

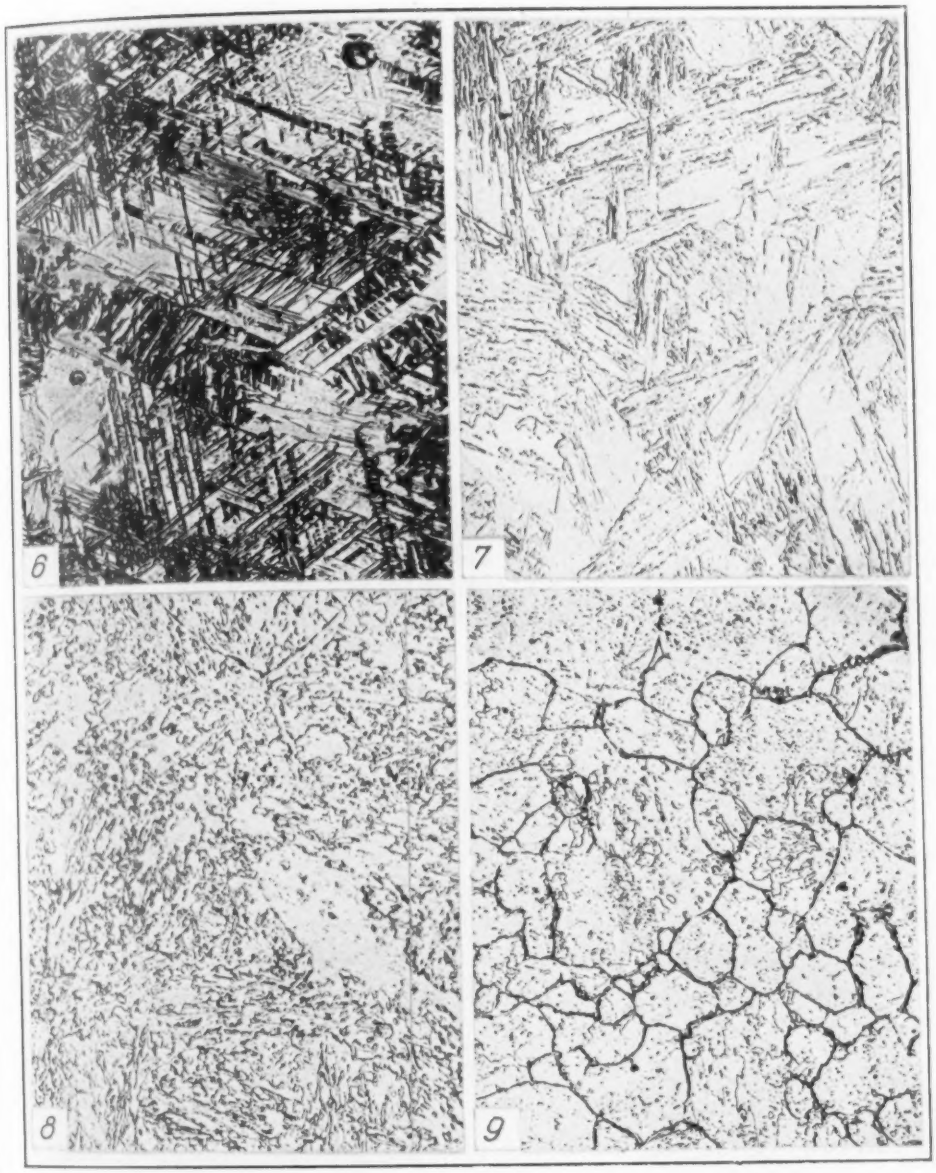


Fig. 6—Manganese 16.0 Per Cent, Carbon 0.02 Per Cent, As-Cast.
Fig. 7—Manganese, 4.4 Per Cent, Carbon 0.01 Per Cent. Quenched from 2100 Degrees Fahr. in Ice Brine.
Fig. 8—Manganese 4.4 Per Cent, Carbon 0.01 Per Cent. Furnace Cooled from 2100 Degrees Fahr.
Fig. 9—Manganese 4.4 Per Cent, Carbon 0.01 Per Cent. Cooled from 1800 Degrees Fahr. Down to Room Temperature in a Week's Time. Etchant 5 Per Cent HNO_3. All Photomicrographs × 250.

indistinct black lines; definite, although small, grains are readily observed. If the same alloy is cooled from 1800 degrees Fahr. (980 degrees Cent.) down to room temperature in a week's time grain

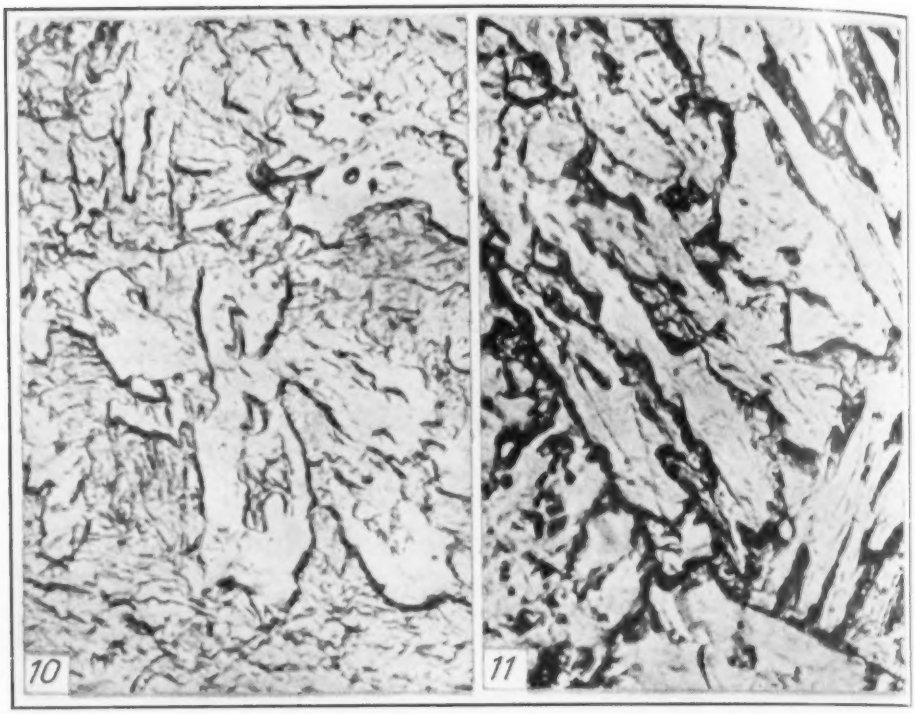


Fig. 10—Manganese 4.4 Per Cent, Carbon 0.01 Per Cent. Sealed in Vacuo, Heated to 1800 Degrees Fahr., Held for One Hour, Quickly Transferred to Another Furnace at 815 Degrees Fahr., Held for 105 Hours, Quenched in Ice Brine.

Fig. 11—Manganese 4.4 Per Cent, Carbon 0.01 Per Cent. Sealed in Vacuo, Heated to 1800 Degrees Fahr., Held for One Hour, Quickly Transferred to Another Furnace at 1020 Degrees Fahr., Held 96 Hours, Ice Brine Quench. Etchant 5 Per Cent HNO_3 Magnified 2000 Diameters.

formation proceeds still further (Fig. 9). Apparently, slow cooling is conducive to formation of grains which are not, perhaps, dissimilar to the same as pictured, for example, in Fig. 2. Since formation of new grains can take place (under normal conditions) only at the temperature of phase change, it would be natural to expect that if any alloy belonging to this group (complete gamma-alpha transformation on cooling) were held at the temperature of transformation for a considerable time, it would be given an opportunity to develop a structure typical for one phase system. An alloy of 4.4 per cent manganese has the gamma to alpha transformation beginning at about 860 degrees Fahr. (460 degrees Cent).[12] At 805 or 825 degrees Fahr. (430 or 440 degrees Cent.) the transformation is in full swing. A sample of this alloy (which, if quenched from 1800 degrees Fahr. (980 degrees Cent.), develops a structure quite similar to one

[12]F. M. Walters and M. Gensamer, "Alloys of Iron-Manganese. Part IV—A Dilatometric Study of Iron-Manganese Binary Alloys, TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 608.

shown in Fig. 7) was sealed in vacuo in glass and after heating to 1800 degrees Fahr. (980 degrees Cent.) was quickly transferred to another furnace at 805-825 degrees Fahr. (430-440 degrees Cent.), where it was held for 105 hours and then rapidly quenched by breaking the glass tube under water (Fig. 10). Another sample of the same alloy received similar treatment except that it was held for 100 hours at 1020 degrees Fahr. (550 degrees Cent.) (Fig. 11). The resulting difference in the structure of two samples is best shown by high power photography, which was used in securing photographs Figs. 10 and 11. Holding a sample within the range of transformation obliterates Widmanstatten tendencies. However, is must be noted that the resulting grain size is quite small.

Hence, it is believed that the Widmanstatten-like pattern in the alloys of this group is due to the formation along crystallographic planes of the metal of minute grains of alpha iron-manganese solid solution at the time of transformation, and without much change in their size preserved through cooling to room temperature. It is at least conceivable that the stresses set up during gamma to alpha change may have some influence on formation of these fine grains. Since the resemblance to large twins was observed in some of these alloys, it is quite probable that both the slippage along crystallographic planes and the twinning are the sources of stresses.

So far the question of solid solubility of manganese in alpha iron has not been discussed. Supposing that the range of solid solubility is very wide (which appears quite likely) and remembering that the rate of diffusion is slow, it is admitted as possible that alpha phase formed at various times of gamma to alpha transformation may be of widely different manganese concentration. Varied action of the etching reagent would then result in a definite structure of Widmanstatten type.

Essentially, these two explanations are not much different. Since no reliable data on solid solubility of manganese in alpha iron are available at present, it is perhaps wise to refrain from further speculations on the subject.

Alloys of lower manganese content,—as for example, one with 1.8 per cent manganese, may even on slow cooling, show isolated grains with complex structure. It is not unlikely that the segregation in the alloy may be the cause of it.

Alloys of the second group, according to dilatometric measurements, undergo gamma to epsilon transformation on cooling and

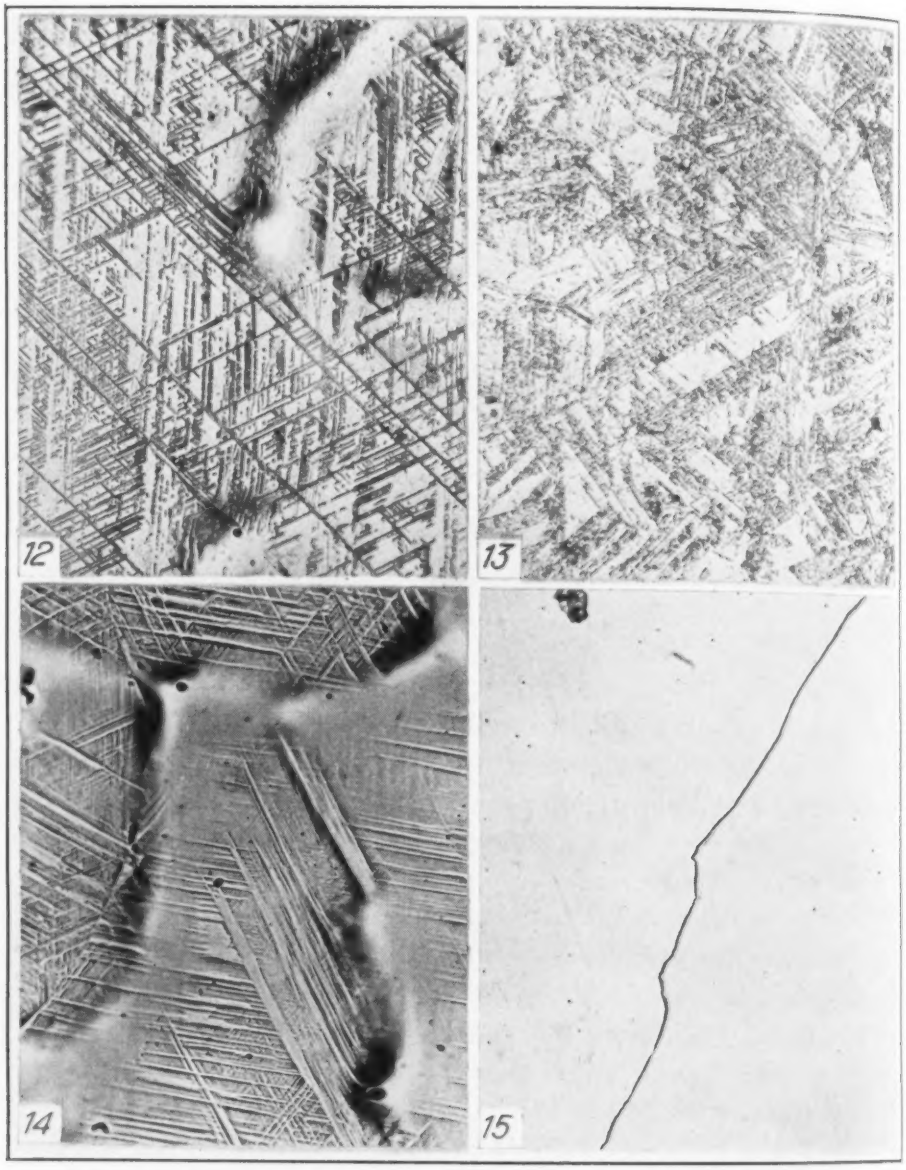


Fig. 12—Manganese 20.4 Per Cent, Carbon 0.02 Per Cent. Heated to 2250 Degrees Fahr., Held 15 Minutes, Ice Brine Quench.

Fig. 13—Manganese 13.1 Per Cent, Carbon 0.01 Per Cent. Furnace-cooled from 2000 Degrees Fahr.

Fig. 14—Manganese 25.8 Per Cent, Carbon 0.02 Per Cent. As-cast.

Fig. 15—Manganese 48.3 Per Cent, Carbon 0.02 Per Cent. Very Slowly Cooled (Over a Week's Time) from 1800 Degrees Fahr. Etchant 5 Per Cent HNO_3. All Photomicrographs × 250.

epsilon phase so formed does not change further to alpha:—X-ray studies indicate the simultaneous presence of various amounts of alpha, epsilon or gamma phase, depending on the heat treatment.

Metallographic studies of this group show the existence of Widmanstatten-type structure under all conditions of treatment (Figs. 6, 12 and 13). In this case it appears certain that the cause for Widmanstatten pattern lies in the formation of infinitely fine grains (as described above) and also in the retention of high temperature phase. In alloys of relatively high manganese content, for example, 13 and 16 per cent, even slow cooling results in retention of considerable quantities of the gamma phase. A complete interpretation of the structures and positive identification of different allotropic forms is quite difficult. Attempts have been made to identify three existing phases (alpha, epsilon and gamma) by means of etching reagents but, so far, without success, due possibly to their fine intermixture. This is especially true of the epsilon phase, which, due to its low temperature of formation, has little chance to develop sufficiently large grain size.

When the percentage of manganese becomes sufficiently high (16 per cent) to suppress altogether the gamma to alpha transformation, the Widmanstatten-type of structure is due to the retained gamma phase and the minute grains of epsilon formed at the cleavage planes of the alloy. Such a structure is shown in Fig. 14.

As was already stated, to Group III belong alloys of 30-60 per cent manganese. In these alloys gamma to alpha transformation is completely suppressed and, consequently, the structure of the alloys becomes of the solid solution type, as is shown in Fig. 15.

The structure of the alloys is, of course, not changed by any heat treatment. Since no phase change occurs in these alloys on heating or cooling, no grain refinement is possible except by mechanical working. Forging of these alloys presents no unusual difficulties and the resulting grain refinement is clearly shown in Fig. 16. Forging of the cast alloys usually reveals a pronounced segregation (Fig. 17) which is completely obliterated only with difficulty.

Increasing manganese content above 60 per cent brings about further changes in microscopic structure. This should be expected since it is at these concentrations (from 60 per cent manganese up) that the presence of alpha and beta manganese phases are disclosed by X-ray analysis.[4, 11]

The structures typical of these alloys are represented by photographs, Figs. 18, 19 and 20. In addition to gamma phase, another constituent appears. This constituent is found in fairly large masses and is easily distinguished by its characteristic appearance:—it is

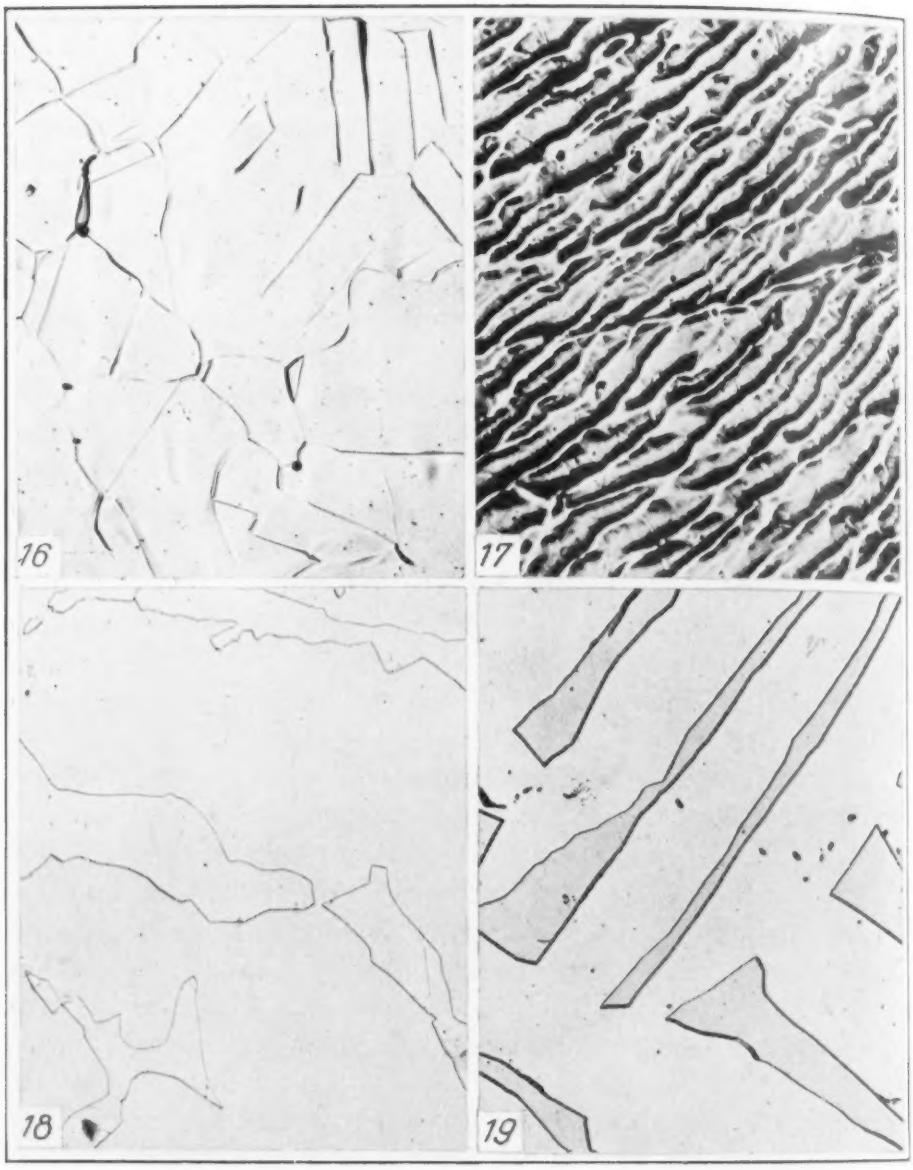


Fig. 16—Manganese 39.9 Per Cent, Carbon 0.01 Per Cent. Forged, Heated to 1800 Degrees Fahr. and Slowly Cooled.
Fig. 17—Manganese 39.9 Per Cent, Carbon 0.01 Per Cent. As-forged.
Fig. 18—Manganese 67.6 Per Cent, Carbon 0.02 Per Cent. As-cast.
Fig. 19—Manganese 90.0 Per Cent, Carbon 0.01 Per Cent. As-cast. Etchant 5 Per Cent HNO_3, All Photomicrographs × 250.

apparenty quite a bit harder than the gamma phase constituting the matrix and unquestionably very brittle. Numerous cracks, stopping abruptly at the gamma phase boundary, are usually present. In fact, the appearance of this constituent closely resembles that of an

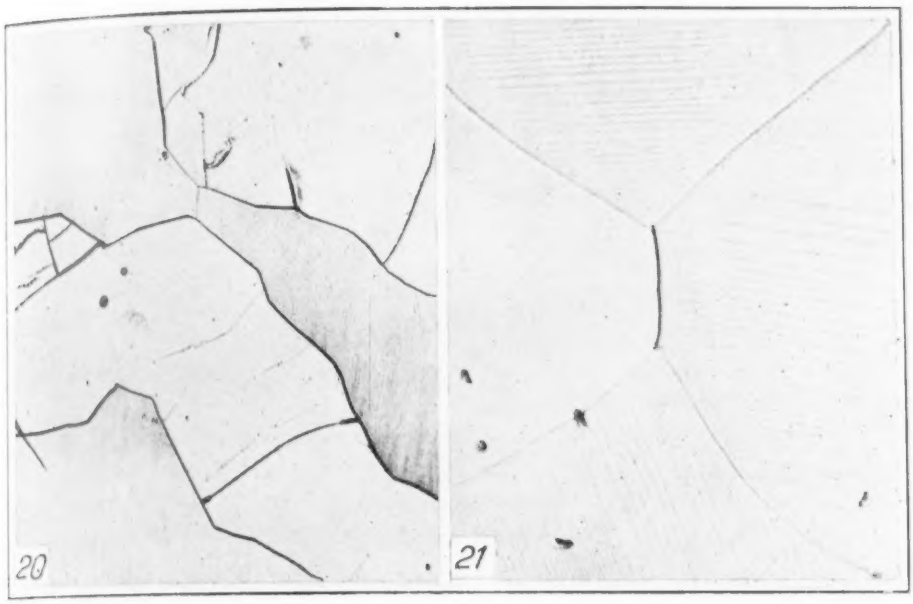


Fig. 20—Manganese 67.6 Per Cent, Carbon 0.02 Per Cent. Heated to 2000 Degrees Fahr., Held 10 Minutes, Furnace-cooled Down to 1200 Degrees Fahr., Ice Brine Quenched from 1200 Degrees Fahr.

Fig. 21—Manganese 90.0 Per Cent, Carbon 0.01 Per Cent. Heated to 2000 Degrees Fahr., Furnace-cooled Down to 1700 Degrees Fahr., Ice Brine Quenched from 1700 Degrees Fahr. Etchant 5 Per Cent HNO_3, Magnified 250 Diameters.

intermetallic compound. Its color is white and the usual etching reagents, such as nitric or picric acids, do not seem to attack it. Its amount increases with the manganese content until finally it may be regarded as a matrix in which the gamma phase is imbedded. Parallel with the increase in the amount of brittle phase, the external shape of gamma grains undergoes a change. These grains now resemble narrow strips, running parallel to each other (Fig 19). It should be noted that while the gamma phase often shows the traces of original ingot segregation, the latter has never been observed in the brittle phase.

In the above discussion the new constituent found associated with gamma phase was deliberately referred to as "brittle" phase or "brittle" constituent. That it is beta manganese phase (solid solution) is quite likely, but a positive metallographic method to differentiate between beta and alpha manganese is still lacking.

Upon heat treatment the alloys just described agree, in general, with the tentative diagram proposed by Öhman,[4] on the basis of X-ray data. For example, any alloy with manganese between 67 and 98 per cent, if quenched from sufficiently high temperatures

(depending on composition. See diagram of Fig. 1), will show gamma manganese (Fig. 21), as should be expected. And on slow cooling of the same alloy, the brittle phase separates out. The microscopic appearance of brittle phase and of gamma phase (except for disappearance of dendritic structure in the latter) is not affected by either annealing or normalizing.

ALLOYS OF IRON, MANGANESE AND CARBON—PART VI

Factors Affecting Transformations in the Binary Iron-Manganese Alloys

By Francis M. Walters, Jr.

Abstract

There are a number of factors which affect the completeness of an allotropic transformation and its temperature range.

This paper gives the effect on the binary iron-manganese alloys of three of these factors; namely, heterogeneity, deformation, and heating rate through the alpha to gamma transformation range.

IT is well known that the character of an allotropic transformation of an alloy, and the temperature at which it occurs are dependent upon a number of circumstances. The rate of cooling, for example, has a marked effect on the temperature of the Ar_1 transformation of ordinary steel. While the rate of cooling has little effect upon the transformations occurring in the binary alloys of iron and manganese, there are other factors which produce marked changes. Of these, three are considered in this paper; (1) heterogeneity, (2) cold work, (3) rate of heating through the transformation range.

Method of Observations

The preparation of the alloys studied has been described elsewhere.[1] In homogenizing, specimens of the alloys were held for eight hours at a temperature 25 to 50 degrees below the solidus. The soaking was carried out in purified helium at atmospheric pressure to prevent loss of manganese as far as possible. The analysis of the

[1]Francis M. Walters, Jr., "Alloys of Iron, Manganese and Carbon—Part I. Preparation of Alloys," Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 577.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. The author, Dr. Francis M. Walters, Jr., a member of the society, is a member of the staff of the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh. Manuscript received July 21, 1932.

alloys and the method of cooling after homogenizing are given below:

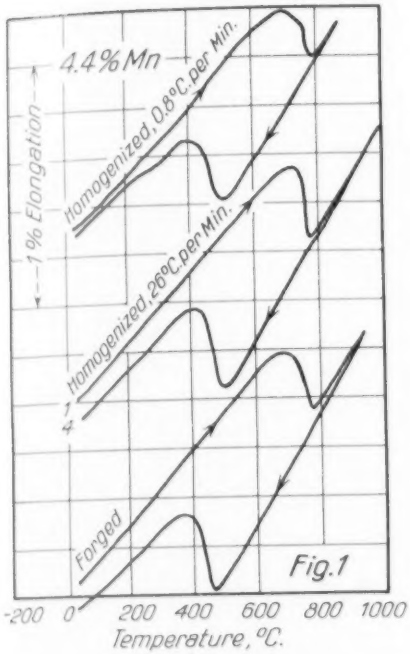
Manganese Per Cent	Carbon Per Cent	Cooling after Homogenizing
4.4	0.020	quenched from 900 degrees Cent. (1650 degrees Fahr.)
7.2	0.014	quenched from 900 degrees Cent. (1650 degrees Fahr.)
10.4	0.015	quenched from 900 degrees Cent. (1650 degrees Fahr.)
13.1	0.029	quenched from 900 degrees Cent. (1650 degrees Fahr.)
16.0	0.021	furnace cooled
20.4	0.017	furnace cooled
25.8	0.014	.....
29.2	0.021	.....

The dilatometer used was that described in previous work.[2] A special furnace was used at slow rates of heating, in order to maintain a uniform increase of temperature without special control of the power input. This furnace had about three-quarters of an inch of calcined infusorial earth between the quartz tube of the dilatometer and the nickel tube on which the heating element was wound.

Of the various methods employed for the study of allotropic transformations, dilatometric data are in general most easily and definitely interpretated, particularly when studied in conjunction with X-ray measurements of the phases involved. For example, with the 4.4 per cent manganese alloys (in curve C of Fig. 1), the decrease in length on heating, which begins at about 650 degrees Cent. (1200 degrees Fahr.) and ends at 770 degrees Cent. (1420 degrees Fahr.), clearly marks the transformation from the body-centered alpha phase to the denser, face-centered gamma phase. Indeed, the difference in length observed dilatometrically when this alloy is in the alpha and when it is in the gamma state, is within experimental error, that predicted by X-ray measurements,[3] when due allowance is made for the difference in thermal expansion of the alloy when in the gamma state and when in the alpha state. From 770 to 935 degrees Cent. (1420-1715 degrees Fahr.) (and higher) the alloy is face-centered and so remains on cooling until 465 degrees Cent. (870 degrees Fahr.) is reached when there begins a sudden increase in length corresponding to the gamma to alpha transformation. That the specimen is somewhat shorter after taking through the heating and

[2]Francis M. Walters, Jr. and M. Gensamer, "Alloys of Iron, Manganese and Carbon—Part IV. A Dilatometric Study of Iron-Manganese Binary Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 608.

[3]M. Gensamer, John F. Eckel, and F. M. Walters, Jr., "Alloys of Iron, Manganese and Carbon—Part III. An X-ray Study of the Binary Iron-Manganese Alloys." TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 599.



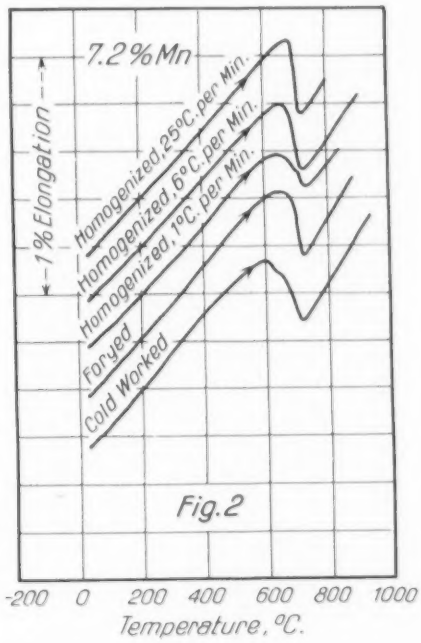


Fig. 1—Heating Curves for 4.4 Per Cent Manganese Alloy.
Fig. 2—Heating Curves for 7.2 Per Cent Manganese Alloy.

cooling cycle shown in Fig. 1 may be due to some or all of the following:

(a) incomplete transformation of gamma to alpha.

(b) relief of strains due to forging or machining.

(c) plasticity of the alloy or the quartz of the dilatometer above the temperature of transformation.

(d) adjustment of the specimen with respect to the apparatus.

(e) extreme plasticity associated with the alpha-gamma transformations.

The heating curve for the 20.4 per cent (A, Fig. 6) shows that at 180 degrees Cent. (355 degrees Fahr.) the specimen underwent a rapid increase in length. This indicates a transformation of epsilon to the more voluminous phase, gamma, since these are the two phases involved in the 20.4 per cent manganese alloy. On cooling, this alloy shows a decrease in length beginning at about 80 degrees Cent., the start of the decomposition of gamma to epsilon. The decrease in length of this alloy due to the formation of epsilon is 0.28 per cent. X-ray measurements indicate that if the transformation were com-

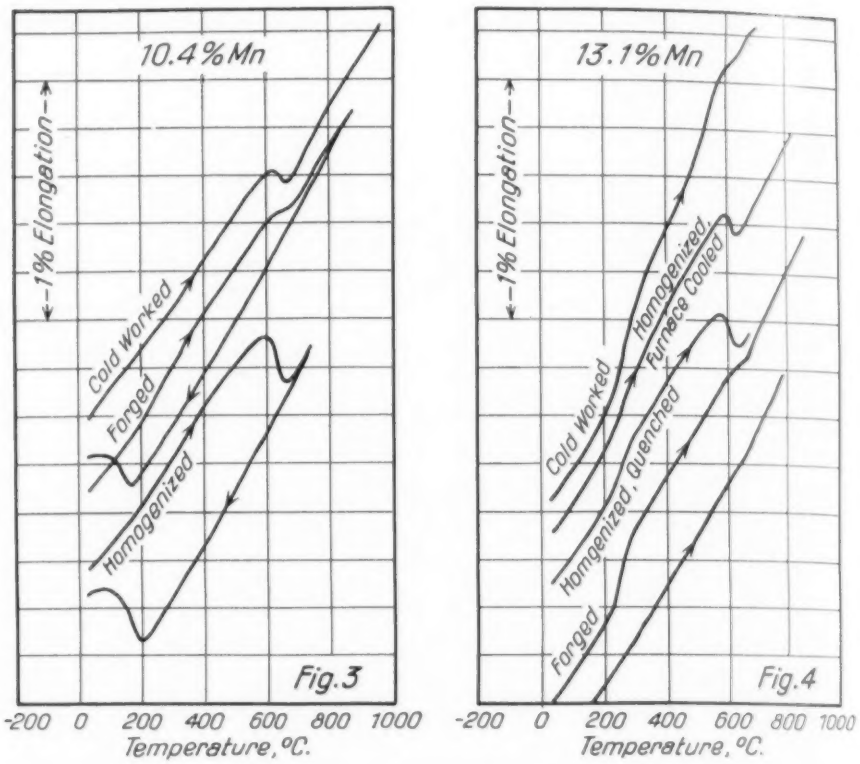
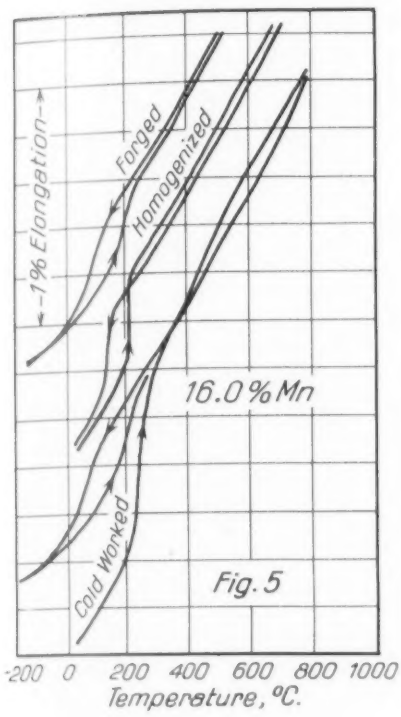


Fig. 3—Heating Curves for 10.4 Per Cent Manganese Alloy.
Fig. 4—Heating Curves for 13.1 Per Cent Manganese Alloy.

plete, the difference in length would be 0.68 per cent. Hence the epsilon transformation is only 41 per cent complete.

Effect of Heterogeneity

It is generally recognized that the alloys of iron and manganese are often heterogeneous. The atomic radii of these two metals are nearly the same and diffusion does not occur at as high a rate as it does in the case of iron and carbon, where the carbon atom is small in comparison with the iron atom. Hence it is necessary to hold the alloys for a long time near the solidus to bring about a marked improvement in homogeneity. Comparing the 4.4 and 7.2 per cent manganese alloys as forged and as homogenized (Figs. 1 and 2), the alpha to gamma and gamma to alpha transformations are completed in a more limited temperature range when the alloys have been homogenized. However, if the homogenized alloys are heated very slowly, the range of temperature over which the transformations occur is greater than for the as forged alloys at moderate heating rates.



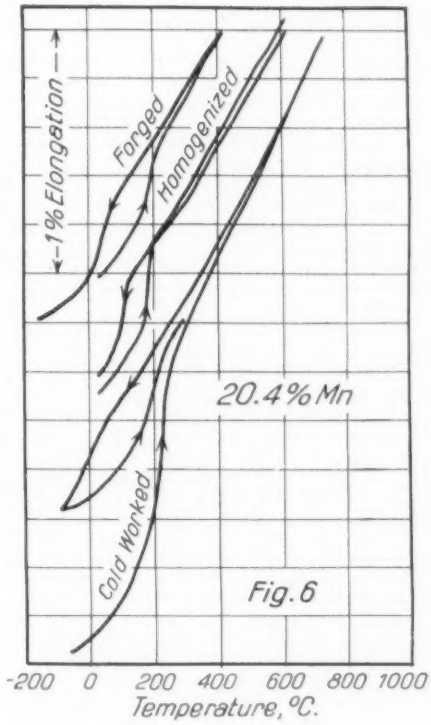


Fig. 5—Heating Curves for 16.0 Per Cent Manganese Alloy.
Fig. 6—Heating Curves for 20.4 Per Cent Manganese Alloy.

The amount of alpha involved in the transformation in the homogenized 10.4-per cent alloy is much greater than in the forged alloy. (Fig. 3). When subsequent runs were made on the forged alloy, it showed larger amounts of alpha as is indicated by the cooling curve.

The 13.1-per cent forged alloy (Fig. 4) showed little alpha present before the first heating, though more was observed on subsequent runs. The homogenized specimen which was slowly cooled from 1325 degrees Cent. (2420 degrees Fahr.) showed less alpha than the homogenized specimen quenched from 900 degrees Cent. (1650 degrees Fahr.). That less alpha was found on slow cooling from 900 degrees Cent. (1650 degrees Fahr.) than on quenching from the same temperature is probably due to the time of homogenizing rather than to the rate of cooling from 900 degrees Cent. (1650 degrees Fahr.). The quenched specimen was homogenized for eight hours while the furnace-cooled specimen was given only five hours.

The epsilon present in the specimens at room temperature was

about the same as in the alloy as forged. Some gamma is retained in the 13-per cent alloy regardless of the treatment.

For the homogenized 16.0 and 20.4-per cent alloys (Figs. 5 and 6) only the gamma-epsilon transformation is observable dilatometrically. For these compositions the narrowing of the transformation ranges due to homogenizing is quite marked. The epsilon to gamma transformation of the homogenized 16-per cent alloy is

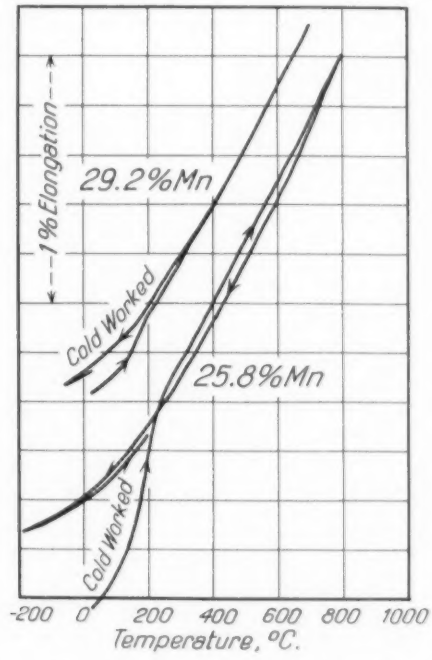


Fig. 7—Heating Curves for 25.8 Per Cent Manganese Alloy.

practically completed within 10 degrees Cent., while in a forged specimen (curve A) it is spread over a hundred degrees or so. Rates of heating and cooling appear to have little effect on the transformation range of the epsilon, although a slow rate serves to sharpen the transformation somewhat. The forged 16-per cent alloy shows 30 per cent epsilon, while 50 per cent of the homogenized alloy is involved in the transformation. The observations on the homogenized alloys indicate that the temperature of the epsilon to gamma transformation is lowered with increasing manganese.

Effect of Cold Work

The study of the effect of cold work upon the transformations

of these alloys was suggested by the theory advanced by Howard Scott[4] to explain why the transformation of gamma to the hexagonal close-packed phase, epsilon, does not go to completion. If a transformation of gamma to the denser phase epsilon remains incomplete because the pressure is relieved through the formation of epsilon, then the application of pressure should increase the amount formed. To test this hypothesis the specimens (referred to as "cold-worked") were given a permanent reduction in length of 5 per cent in a testing machine.

The cold-worked 20.4-per cent alloy (Fig. 6) showed on the first heating an increase in length of 0.65 to 0.70 per cent. This length change indicates that the alloy had been completely transformed to epsilon. This transformation was, however, not quite complete in the case of the 16.0 per cent alloy (Fig. 5) and another cold-worked specimen gave an indication of the presence of a small amount of alpha. The curve shown for the 16.0-per cent alloy is for a sample which had been cold-worked five months before the observations were made.

Seventy per cent of epsilon was formed by cold working the 25.8-per cent alloy (Fig. 7), though only 12 per cent was observable in a forged specimen. No epsilon is detectable dilatometrically in the 29.2-per cent alloy and cold work evoked only 17 per cent.

The cold-worked 13.1-per cent specimen (Fig. 4) does not have much more epsilon than the forged alloy, unless it is assumed that the abnormal expansion above 350 degrees Cent. (660 degrees Fahr.) is due to the epsilon to gamma transformation, rather than the formation, in this temperature range of alpha from the gamma disturbed by cold work. At least half the as forged alloy is gamma at room temperature.

Cold work has disturbed the alpha to gamma transformation of the 7.2-per cent alloy (Fig. 2), lowering the temperature at which the transformation begins and raising slightly the temperature at which it is completed. The effects of cold work on the transformation in the iron-manganese alloys may be due either to plastic deformation or to stress. It would be of much interest to subject these alloys to a volume stress.

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[4]Howard Scott, "Transformational Characteristics of Iron-Manganese Alloys." American Institute of Mining and Metallurgical Engineers, Technical Publication No. 435, Sept. 1931.

Rate of Heating

The effect of a slow rate of heating on the alpha to gamma transformation of the 4.4-per cent manganese alloys is shown in Fig. 1. The rate of the alpha expansion falls off at 600 and at 695 degrees Cent. (1110 and 1285 degrees Fahr.) the alloy begins to shorten. Although the heating rate was kept uniform, at 770 degrees Cent. (1420 degrees Fahr.), the rate of gamma formation increased. The transformation is completed at a slightly higher temperature than when the alloy is taken through the transformation range rapidly. On cooling, the gamma to alpha transformation is not completed until the temperature is less than 200 degrees Cent., while after a rapid heating through the alpha to gamma range, it is practically complete at 400 degrees Cent. (750 degrees Fahr.).

Heating at a slow rate affects the alpha to gamma transformation of the 7.2-per cent manganese alloy similarly, but to a greater degree. (Fig. 2). Although less alpha is transformed to gamma in the 10.4 and 13.1-per cent alloys, yet the temperature range is greater than in the case of the 4.4-per cent and 7.2-per cent alloys, even at the same rate of heating. It is possible that while 25 degrees Cent. a minute is a rapid rate of heating for 7 per cent manganese it is a slow rate for 10 per cent. The temperature at which alpha begins to form is lowered by slow heating because time is given for formation of grains high enough in manganese to transform to gamma at the lower temperature. The discontinuity in the alpha to gamma transformation at 770 degrees Cent. (1420 degrees Fahr.) in the 4.4-per cent manganese alloy at a slow rate of heating probably marks the limit of the temperature at which the nascent gamma takes manganese from the untransformed alpha. The 7.2-per cent alloy shows a similar break at 710 degrees Cent. (1310 degrees Fahr.) and the 10.4 per cent alloy at 630 degrees Cent. (1165 degrees Fahr.).

Summary

Dilatometric observations on binary iron-manganese alloys show the following:

1) The alpha-gamma transformation range on heating and cooling is increased by a slow heating rate.

2) That the alloys are rendered more homogeneous by holding several hours at temperatures near the solidus is indicated by a nar-

rowing of both the alpha-gamma and the epsilon-gamma transformation ranges.

3) In alloys containing 16 to 30 per cent manganese the amount of the epsilon phase is increased by deformation and the transformation is substantially complete in the 20-per cent alloys.

ALLOYS OF IRON, MANGANESE AND CARBON—PART VII

*Influence of Carbon on Thirteen Per Cent Manganese Alloys**

By Cyril Wells and Francis M. Walters, Jr.

Abstract

The work reported in this paper is part of a comprehensive investigation of the pure alloys of iron, manganese and carbon. The thirteen per cent manganese section of the ternary phase diagram has been determined by the examination of specimens brought to substantial equilibrium at crucial temperatures. It was found that a soak of at least eight hours near the solidus was necessary to bring about a satisfactory distribution of manganese in the forged alloys. Epsilon as well as alpha was found as a low temperature decomposition product.

THE phase diagram given in Fig. 1 is the cross section of the ternary iron-carbon-manganese system for thirteen per cent manganese. In its determination were used the very pure alloys prepared from distilled manganese and vacuum melted electrolytic iron.

Above ABC there exists only one phase, the gamma solid solution containing iron, manganese and carbon (austenite).

As line CB is crossed on cooling, carbides are separated in the region CBE.

In the region CBE there are two phases, gamma solid solution and carbides. The carbides occurring in iron-manganese alloys containing about 1 per cent carbon and between 5 and 13.4 per cent manganese, when separated and analyzed, have been found to contain about 7 per cent carbon and 22 per cent manganese.[1] In the cementite found in iron-manganese alloys, manganese atoms replace iron atoms, at least up to 22 per cent. Whether the manganese carbides, Mn_4C and Mn_7C_3, occur in the 13 per cent alloys is not known. If the carbides contain a higher percentage of manganese than the alloy as a whole, then the matrix will contain a lower percentage.

*This paper was condensed from a thesis submitted by Cyril Wells to the College of Engineering of the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science, Pittsburgh, June, 1932.

[1]J. O. Arnold and A. A. Read, "The Chemical and Mechanical Relations of Iron, Manganese, and Carbon," *Journal*, Iron and Steel Institute, Vol. 81, 1910, p. 176.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Manuscript received June 6, 1932.

This is confirmed by the thermal analysis of the carbon alloys which show a higher transformation temperature than the low carbon alloys. (Fig. 2.)

Since the carbides which separate as the alloys are cooled through the region CBE impoverish the remaining solid solution in manganese as well as in carbon, the alpha to gamma transformation, indicated by the line BE, is raised as the carbon increases.

The raising of the line DB with increasing carbon content shows

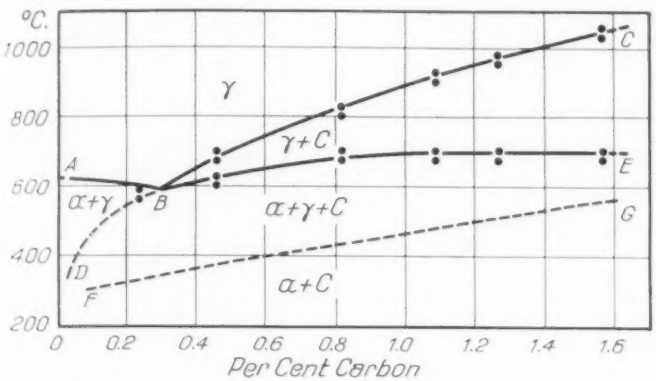


Fig. 1—13 Per Cent Manganese Section of the Ternary Diagram of Alloys of Iron, Manganese and Carbon.

that when the line AB is crossed on cooling, the gamma remaining after the separation of alpha is enriched in carbon and manganese.

On cooling just below the line BE, the three phases, alpha, gamma, and carbides, exist in equilibrium. Cooling further separates more alpha and carbide phases until, finally, all the gamma is decomposed, as indicated by the line FG. This line has not been determined experimentally, but is drawn in to indicate that, at some temperature, the gamma solid solution becomes unstable. Below FG the stable phases are alpha solid solution and carbides.

Passing below BD, from the region ABD, carbides are separated, in addition to the alpha constituent, and, finally, the line FG is again approached where the last gamma disappears. The point B indicates the composition of the pearlite which forms at that temperature. When an alloy of eutectoid composition is held just below the eutectoid temperature only a limited amount of the gamma solid solution can transform to pearlite, since formation of this pearlite alters the composition of the remaining gamma, and hence the temperature at which it transforms to pearlite.* Accordingly,

*In a three component system the quantity and composition of any one phase in a

pearlite, which is formed in the course of a slow cooling through the three phase region has a variable composition. In this connection may be noted the difference in the structure of the pearlite formed during an extremely slow cooling (Fig. 3) and that formed in the same alloy on holding at a constant temperature (Fig. 4)

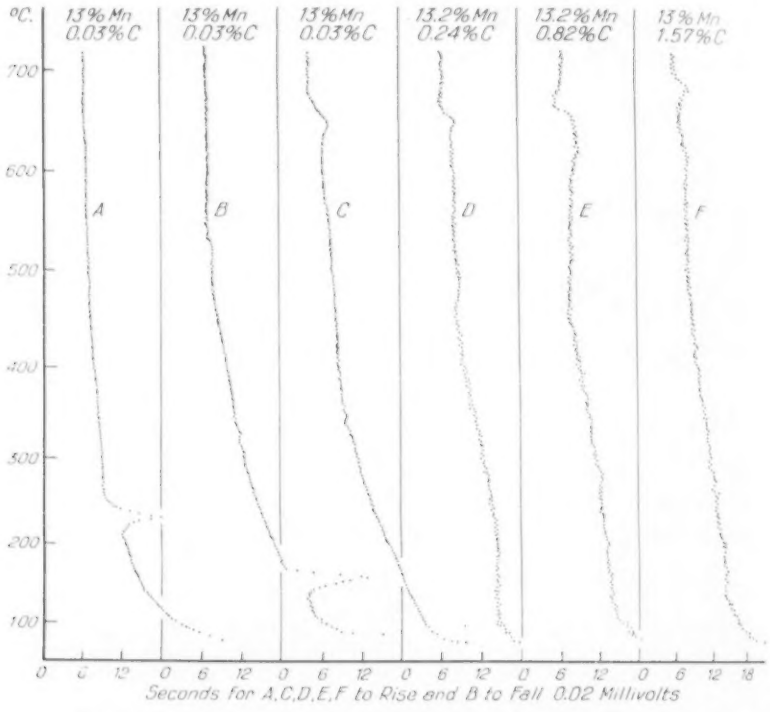


Fig. 2—Curves A and B, Alloys "as-forged." Heated and Cooled at 15 Degrees Cent. Per Minute. Note the Epsilon-gamma and Gamma-Epsilon Transformations, and the Comparatively High Reversibility of these Alloys.

Curves C, D, and E, Indicate Thermal Disurbances Due to Alpha to Gamma Transformations. Alloys Cold-worked (20 per cent reduction by hammering), were Soaked 56 Hours at 550 Degrees Cent. and Furnace Cooled in 12 Hours; Heated in Gradient Furnace at 15 Degrees Cent. per Minute.

Curve F, Note the Raised Alpha to Gamma Transformation due to Previous Separation of Carbides. Before Making Thermal Analysis, Alloy Containing 1.57 per cent Carbon was Furnace Cooled over a Week's Time from 980 Degrees Cent. to Room Temperature.

just under the line BE. A further illustration of this is to be found when a slowly cooled specimen is heated to a temperature within the three phase region. Only part of the pearlite transforms, usually that toward the edge. (Fig. 5.)

The proportions and compositions of the phases in any two or

three phase region are fixed by the temperature, because each of the three phases is then saturated with the three components. However, since the solubility limits of each phase vary with temperature, both the quantities and compositions of the phases vary accordingly, as the temperature is changed.

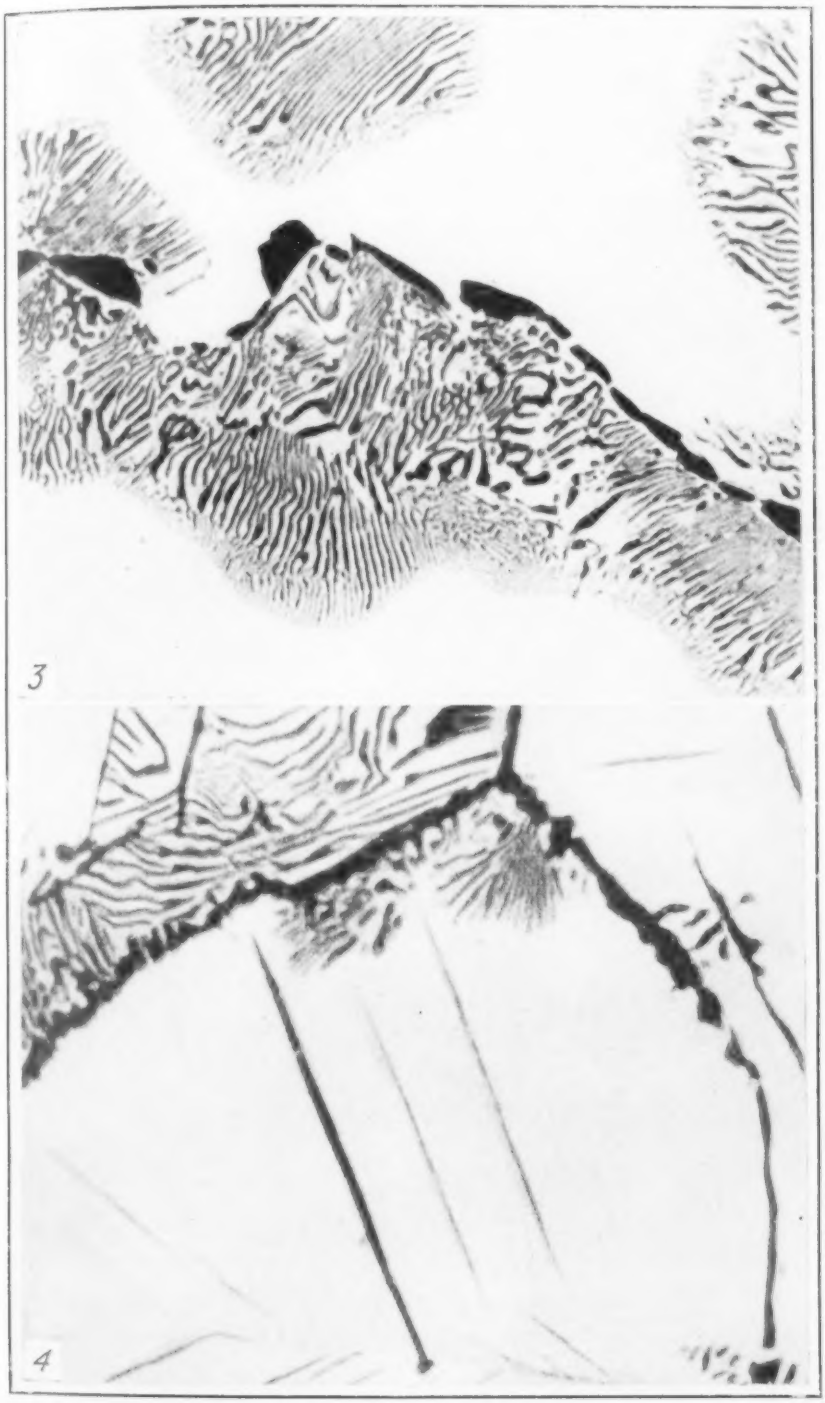


Fig. 3—12.0 Per Cent Manganese. 1.09 Per Cent Carbon. Three Week's Cool from 980 Degrees Cent. Etchant, Sodium Picrate. × 2000. Shows Pearlite and Excess Carbides at the Grain Boundary. Note the Finer Structure, Especially at the Edges of the Pearlite.

Fig. 4—12.0 Per Cent Manganese. 1.09 Per Cent Carbon. Held 67 Hours at 600 Degrees Cent. Etchant, Sodium Picrate. × 2000. Shows Pearlite, Excess Carbides in Grain Boundaries, and Carbides in the Cleavage Planes, Giving a Needle-Like Constituent.

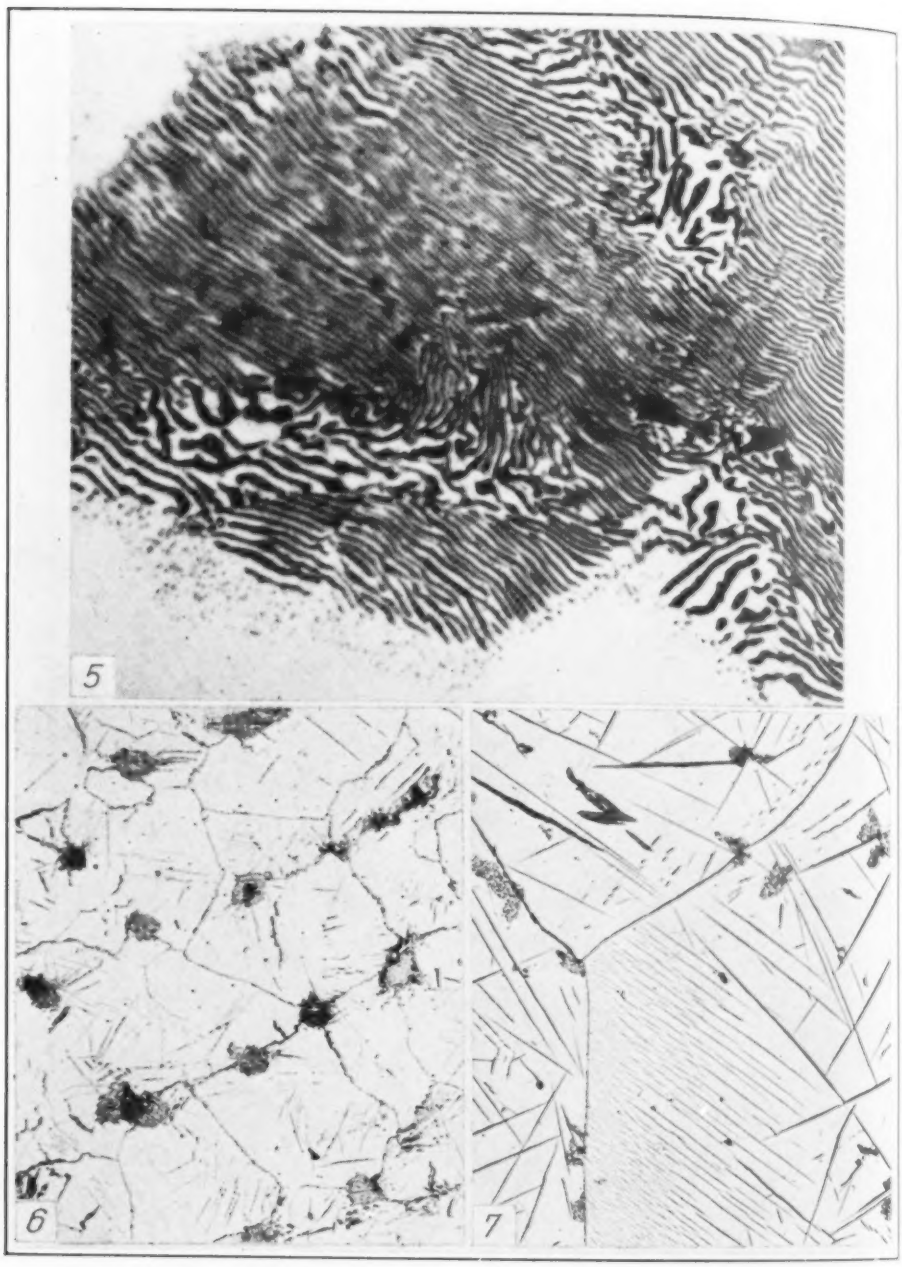


Fig. 5—12.8 Per Cent Manganese. 0.46 Per Cent Carbon. Week's Cool from 980 Degrees Cent. (Reheated to 600 Degrees Cent. for Half an Hour). Etchant, Sodium Picrate. × 2000. Note the Disappearing Fringe at the Edge of the Pearlite. Most of the Pearlite has Remained Unchanged.

Fig. 6—13.0 Per Cent Manganese. 1.57 Per Cent Carbon. Forged. Etchant, Sodium Picrate. × 250. Note the Evidence for Dendritic Segregation.

Fig. 7—13.0 Per Cent Manganese. 1.57 Per Cent Carbon. Homogenized at 1150 Degrees Cent. for 12 Hours, Quenched 1100 Degrees Cent., Reheated to 550 Degrees Cent., Held Two Hours, Quenched. Reheated to 700 Degrees Cent., Held Two Hours, Quenched. Etchant, Sodium Picrate. × 250. Shows an Even Distribution of Carbides Due to the Homogenizing Treatment. Note the Spheroidized Carbides in Those Areas Which Were Formerly Lamellar Pearlite.

three-phase regions are unknown, but even if they are known, they could not be represented on the diagram shown in Fig. 1, since it is not a pseudo-binary plane.

It is assumed that the only equilibrium phases below the line FG are alpha and carbides. It must be pointed out, however, that under ordinary conditions whenever the gamma phase is low enough in carbon it transforms on cooling to epsilon as well as to alpha. A comparison between this diagram, based on the pure alloys and one recently published for alloys of commercial purity,[2] shows general agreement. Considerable differences in the carbide solubility line were noticed.

Experimental Procedure

The alloys used to determine the diagram shown in Fig. 1, were melted under argon. Distilled manganese and vacuum melted electrolytic iron were used in their preparation and they contain only traces of impurities.[3]

Table I

Alloy number	Carbon Per cent	Manganese Per cent	Homogenizing Degrees Cent.	Hours
A-7	0.03	13.1	1325	5
A-23	0.24	13.2	1325	5 and 12
A-42	0.46	12.8	1250	5 and 12
A-36	0.82	13.2	1250	5 and 12
A-43	1.09	12.0	1150	5
A-45	1.27	13.3	1150	5 and 12
A-16	1.57	13.0	1150	12

The ingots, approximately 3.5 inches in diameter, were forged into rods about one-half or five-eighths of an inch in diameter, giving a reduction of from 90 to 97 per cent. For crucial experiments, the forged alloys were given a thorough homogenizing treatment (Table I). To minimize any change of chemical composition, due to oxidation or demanganization, the heating was carried out in purified helium at atmospheric pressure.

That the homogenizing treatment given was successful in reducing the heterogeneity of the alloy as forged was indicated in two ways. The epsilon to gamma transformation range in the 16 per

[2] E. C. Bain, E. S. Davenport and W. S. N. Waring, "The Equilibrium Diagram of Iron-Manganese-Carbon Alloys of Commercial Purity." Technical Publication No. 467, American Institute of Mining and Metallurgical Engineers, Fig. 8, page 13.

[3] F. M. Walters, Jr., "Alloys of Iron, Manganese and Carbon. Part I." Transactions, American Society for Steel Treating, Vol. XIX, 1932, p. 577.

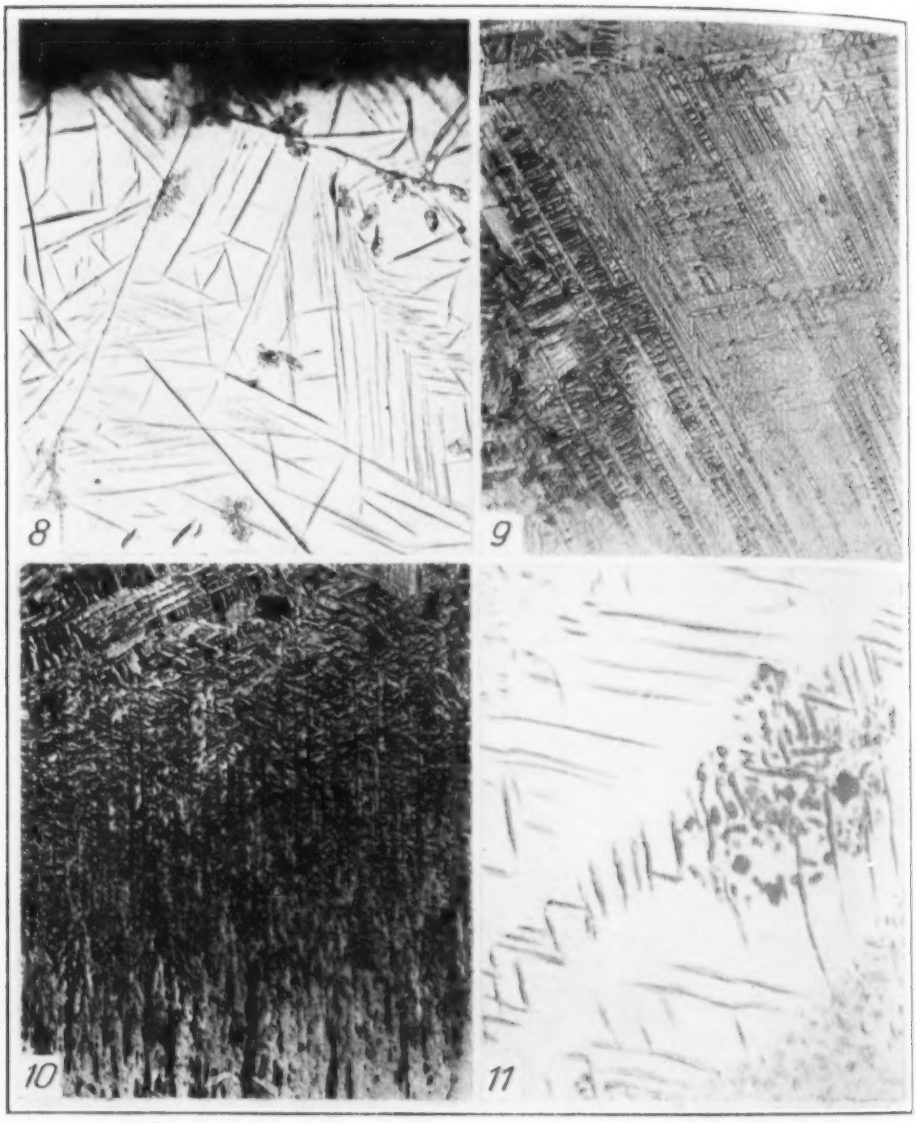


Fig. 8—13.0 Per Cent Manganese. 1.57 Per Cent Carbon. Homogenized at 1150 Degrees Cent., for Twelve Hours, Quenched 1100 Degrees Cent., Reheated to 550 Degrees Cent., Held There Two Hours, Quenched, Reheated to 700 Degrees Cent., Held There Two Hours, and Quenched. Etchant, Sodium Picrate. × 250. Note the Above Alloy Shows Practically No Decarburization Towards the Edge (Compare With Fig. 7).

Fig. 9—16 Per Cent Manganese. 0.02 Per Cent Carbon. Homogenized at 1325 Degrees Cent. for 8 Hours, Cooled to 900 Degrees Cent., and Quenched. Etchant, 4 Per Cent Nital. × 250. This Structure is Typical of the 16.0 Per Cent Manganese Alloy After the Above Treatment

Fig. 10—16.0 Per Cent Manganese. 0.02 Per Cent Carbon. Homogenized at 1325 Degrees Cent. for 8 Hours, Cooled to 900 Degrees Cent., and Quenched. Etchant, 4 Per Cent Nital. × 250. Near the Outside of the Sample. This Structure Compared with Fig. 12 Indicates that Some Demanganization Has Taken Place.

Fig. 11—12.0 Per Cent Manganese. 1.09 Per Cent Carbon. Homogenized at 1250 Degrees Cent. for 5 Hours, Furnace-Cooled, Reheated to 1050 Degrees Cent., Quenched, Reheated to 575 Degrees Cent. for Two Hours and Quenched. Reheated to 660 Degrees Cent. for Two Hours and Quenched. Etchant, Sodium Picrate. × 2000. Shows the Distribution and Size of Carbides Produced for the Determination of Carbide Solubility.

cent manganese, 0.02 per cent carbon alloy was reduced from 100 degrees Cent. in the forged alloys to 10 degrees Cent. after homogenizing.[4] In the case of the alloys containing carbon, the improvement in homogeneity is indicated by the uniformity of the carbide distribution. The dendritic segregation shown in Fig. 6 has been entirely removed by the treatment given (Fig. 7). Since the higher manganese content of the carbides makes it probable that the carbon is concentrated in the manganese-rich areas, such a distribution of carbides as that shown in Fig. 7 may be taken as evidence of a satisfactory distribution of manganese as well.

Five hours was found to be insufficient to bring about homogeneity in the alloy containing 0.46 per cent carbon, but twelve hours was sufficient to remove all but a few traces of especially persistent heterogeneity.

After the high temperature treatment in helium, the surface showed little or no indication of oxidation. A comparison of the carbide distribution at the center (Fig. 7) and at the outside of a specimen (Fig. 8) indicates that very little decarburization had occurred during homogenizing. However, a low carbon 16 per cent manganese specimen which had been homogenized showed to a depth of 0.008 of an inch a structure which was suggestive of loss of manganese. The structure of the inside of the sample (Fig. 9) is typical, but the structure observed near the outside (Fig. 10) is indicative of lower manganese content.

Determination of Carbide Solubility Line

To determine the temperature at which all the carbon goes into solution, the alloys were given a heat treatment which would give throughout the alloy a uniform distribution of carbides of a rather small particle size. By thus limiting the amount of diffusion necessary for the solution of the carbides, the time required to attain equilibrium should be decreased.

The homogenized alloys which had been furnace cooled were held in vacuo at 1050 degrees Cent. (1920 degrees Fahr.) for 30 minutes to secure a uniform distribution of carbon and then quenched. These alloys were then reheated to 500 degrees Cent. (930 degrees Fahr.) and held long enough to precipitate carbides of a width less than 0.002 millimeters. The 1.57 and 1.27 per cent carbon alloys

[4] F. M. Walters, Jr., "Alloys of Iron, Manganese and Carbon. Part VI. Factors Affecting Transformations in the Binary Iron-Manganese Alloys." Fig. 5.

were held for twenty minutes, the 1.09 and 0.82 for one hour and the 0.46 for twelve hours. To produce visible carbides in the 0.24 per cent carbon alloy it was necessary to cold work the specimen, cool it in liquid nitrogen and soak for a week at 550 degrees Cent. (1020 degrees Fahr.). In spite of having taken more than 200 photomicrographs, when the time came for writing this paper, the most typical photomicrograph that could be found to show the distribution and particle size of the carbides was the one shown in Fig. 11.

The specimens with the controlled carbide precipitation were held for two hours at temperatures near those at which the carbon is completely soluble. A thermocouple inserted in a saw cut in each specimen served a double purpose: it indicated the temperature of the sample (in which variation of temperature was less than plus or minus 5 degrees Cent.) and it also served as a means of handling the sample, so the time required to get the samples from the furnace and into the water was of the order of one second and the temperature drop only two or three degrees. The results of the quenching experiments for the determination of the line BC are given in Table II.

Table II

Alloy number	Carbon Per cent	Manganese Per cent	Time at Temp. Hrs.	Temp. at which carbides are present °C	Temp. at which no carbides are present °C
A-23	0.24	13.2	2	565	590
A-42	0.46	12.8	2	675	700
A-36	0.82	13.2	2	800	825
A-43	1.09—	12.0	2	900	925
A-45	1.27	13.3	2	950	975
A-16	1.57	13.0	2	1025	1050

For the final determination of the line BC, the samples were cut in two and the cut surface examined.

Upper Limit of the Alpha Phase

The criterion for the determination of the temperature of the upper limit of the alpha phase was whether or not pearlite was formed in a partially decomposed specimen. This method was not applicable to alloys which contained less than 0.46 per cent carbon, and in the case of the 0.03 per cent carbon alloy, the disappearance of alpha was determined dilatometrically. In preparation for soaking at crucial temperatures homogenized specimens of the alloys were heated in vacuo to 1050 degrees Cent. and cooled to 750 degrees Cent. in six hours, and quenched. This treatment precipitated car-

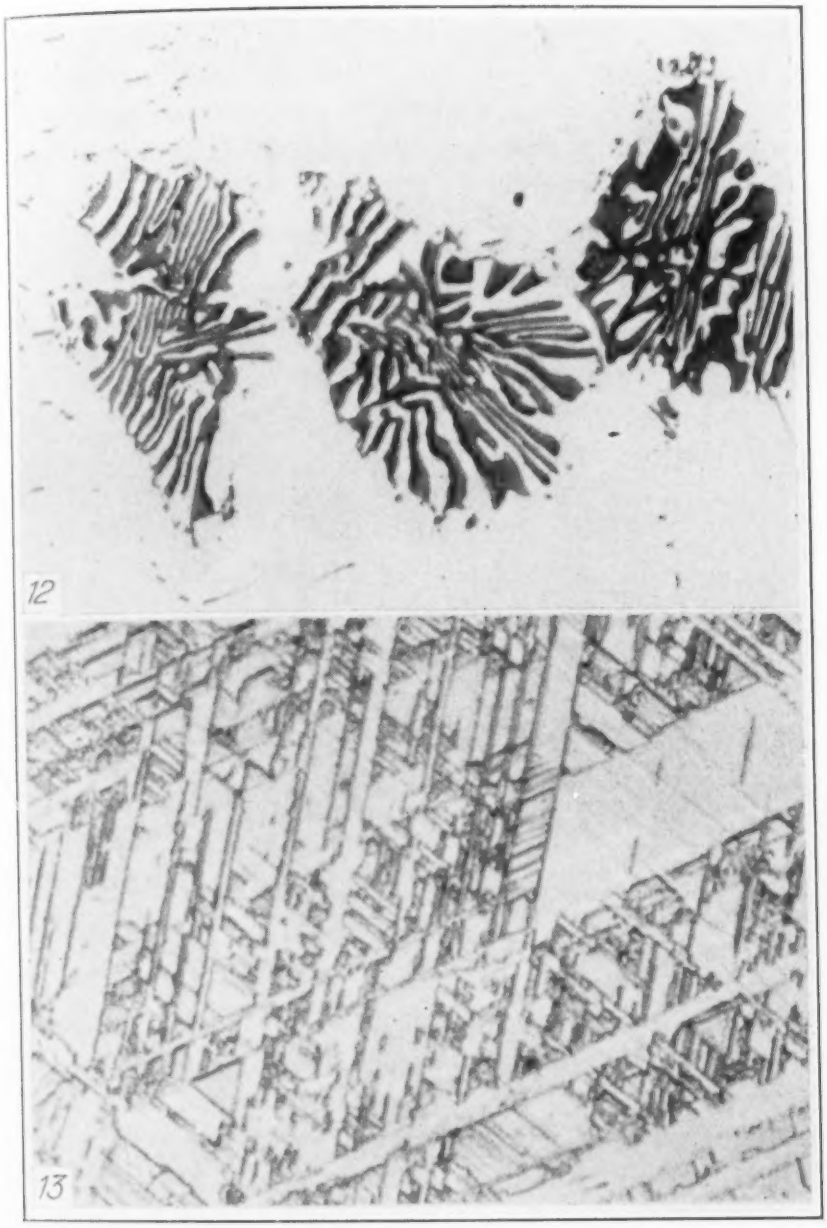


Fig. 12—13.0 Per Cent Manganese. 1.57 Per Cent Carbon. Homogenized 12 Hours at 1150 Degrees Cent., Furnace-Cooled, Reheated to 1050 Degrees Cent., Cooled to 775 Degrees Cent. in Six Hours, Held There for 15 Minutes and Quenched. Cold-Worked 7 Per Cent Reduction by Compression. Reheated to 675 Degrees Cent. for One Week and Quenched. Etchant, Sodium Picrate. × 2000. Shows Coarse Well Developed Pearlite.

Fig. 13—16.0 Per Cent Manganese. 0.02 Per Cent Carbon. Furnace-Cooled from 750 Degrees Cent. (in Helium). Etchant, 4 Per Cent Nital. × 2250. Shows the Widmanstatten Type of Structure Well Developed. The Alloy Contains Epsilon and Untransformed Gamma.

bides and permitted some diffusion to occur, especially in the high carbon alloys. The specimens were reduced 7 or 8 per cent in length in a testing machine, to accelerate the reactions in the subsequent soaking. These specimens, which were about half an inch in diameter and an inch and a quarter long, were cut into five parts. One piece of each alloy was inserted in a pyrex tube which was sealed off after evacuation. Sets of the specimens were soaked for a week at 600, 625, 650, 675, and 700 degrees Cent. The temperature variation was less than plus or minus 5 degrees Cent. The specimens were quenched from the soaking temperatures, cut in two and examined for pearlite. In general, the pearlite formed by this treatment was of the lamellar type and well defined when sodium picrate was used as the etchant (Fig. 12). However, in one or two cases, it was necessary to use 4 per cent nital in conjunction with the sodium picrate. The results are given in Table III.

Table III

Alloy Composition Carbon Per cent	Manganese Per cent	Temperature at which pearlite is observed. °C	Temperature at which pearlite is not observed. °C
0.46	12.8	600	625
0.82	13.2	675	700
1.09	12.0	675	700
1.27	13.3	675	700
1.57	13.0	675	700

The upper limit for alpha in the 0.24 per cent carbon alloy has not been determined.

Decomposition Products of the Gamma Phase

When the gamma phase in the 13 per cent alloys is low enough in carbon, it has two possible products of decomposition, alpha and epsilon. Alpha is body-centered cubic and epsilon, hexagonal close packed. The volume per lattice point is greatest for alpha and least for epsilon so that the decomposition of gamma to alpha is accompanied by an increase in volume but the decomposition to epsilon results in a decrease in volume.

The gamma to alpha transformation temperature of the binary alloys decreases rapidly with the addition of manganese: 13 per cent manganese depresses it to about 100 degrees Cent. and when the manganese content is 16 per cent the transformation does not occur even at the temperature of liquid nitrogen. The temperature of the reverse transformation alpha to gamma, is affected less, the trans-

formation in the 13 per cent alloy being complete at 640 degrees Cent. (1185 degrees Fahr.). This transformation is characterized by a large degree of hysteresis.

Epsilon is found in the binary alloys containing ten to thirty per cent manganese. With sixteen per cent or more manganese it

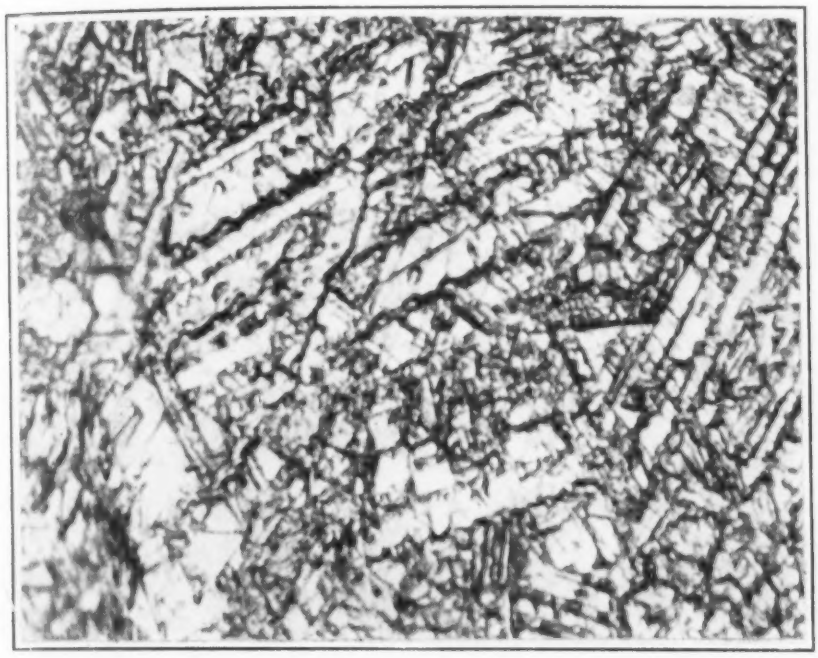
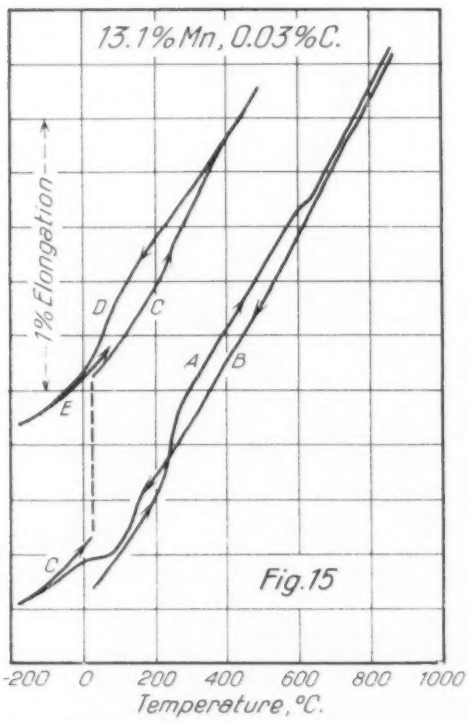


Fig. 14—13.1 Per Cent Manganese. 0.03 Per Cent Carbon. Furnace-Cooled from 900 Degrees Cent. Etchant, 4 Per Cent Nital. × 2250. The Structure is Very Complex Due to the Presence of all Three Phases, Gamma, Alpha and Epsilon. There is Some Trace of the Widmanstatten Pattern Typical of the Higher Manganese Alloys, in Which Only the Gamma to Epsilon Transformation is Involved.

is the predominant decomposition product of gamma; in the ten per cent alloy it is only a minor constituent. However, in the thirteen per cent manganese alloy alpha and epsilon are of about equal importance. In this alloy the gamma to epsilon transformation occurs at about 150 degrees Cent. and the epsilon to gamma at 250 degrees Cent., thus the hysteresis associated with the epsilon transformation is of the order of 100 degrees Cent. compared with 500 degrees Cent. in the case of the alpha transformation.

The transformation of gamma to epsilon is incomplete under ordinary conditions and when no alpha is formed a clearly defined Widmanstatten pattern is formed (Fig. 13). In the case of the as forged low carbon thirteen per cent manganese alloy, epsilon



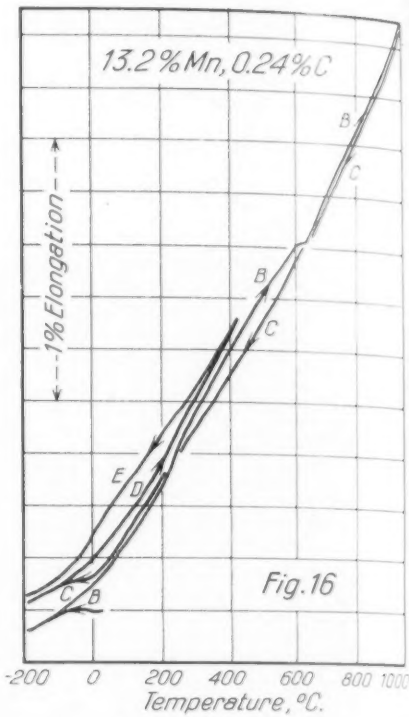


Fig. 15—13.1 per cent Manganese, 0.03 per cent Carbon "as-forged." Heating and Cooling Rate 10 Degrees Cent. per Minute.
Fig. 16—13.2 per cent Manganese, 0.24 per cent Carbon "as-forged." Heating and Cooling Rate 10 Degrees Cent. per Minute.

begins to form on cooling at about 120 degrees Cent., and the gamma to alpha transformation at about 80 degrees Cent., the two transformations then proceeding simultaneously to room temperature. Consequently, the structure of the low carbon thirteen per cent alloy shows evidence of both epsilon and alpha transformations (compare Fig. 13 where only gamma-epsilon change occurs with Fig. 14 where both changes occur simultaneously).

No etching reagent has been found by means of which epsilon and alpha grains may be differentiated. Since epsilon transforms to gamma below 300 degrees Cent., grain growth is very slow and the probability of discovering such an etchant seems remote.

Epsilon has been considered by some investigators to be a transition phase; but there are several reasons for believing it to be stable:

(1) The high reversibility of the transformation in the low carbon alloys
(2) Epsilon has a smaller volume than the other iron-manganese phases

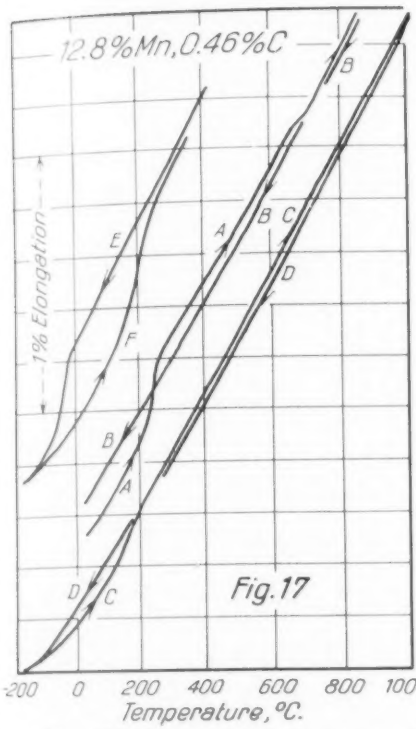


Fig. 17

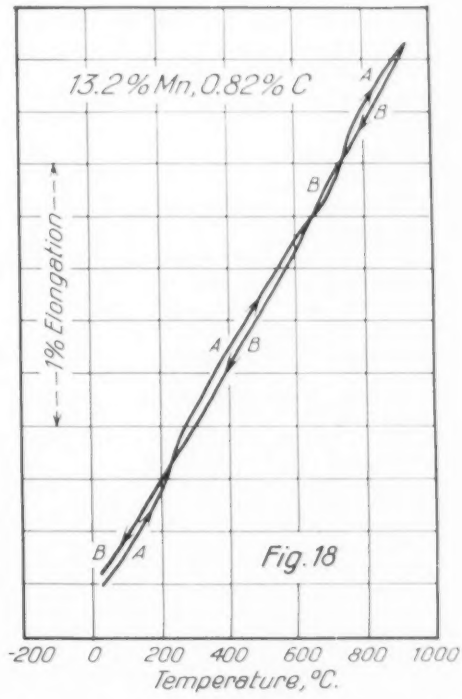


Fig. 18

Fig. 17—12.8 per cent Manganese, 0.46 per cent Carbon. Homogenized (Heated for Five Hours at 1250 Degrees Cent., Furnace-cooled). Cold-worked 7 per cent by Compression and Soaked for Two Weeks at 550 Degrees Cent. E-F, Large Amount of Epsilon after a Further Two Weeks at 550 Degrees Cent.

Fig. 18—13.2 per cent Manganese, 0.82 per cent Carbon. Homogenized (Five Hours at 1250 Degrees Cent., Furnace-cooled). Cold-worked and Soaked at 550 Degrees Cent. for Fifty Hours. Heating and Cooling Rate 10 Degrees Cent. per Minute.

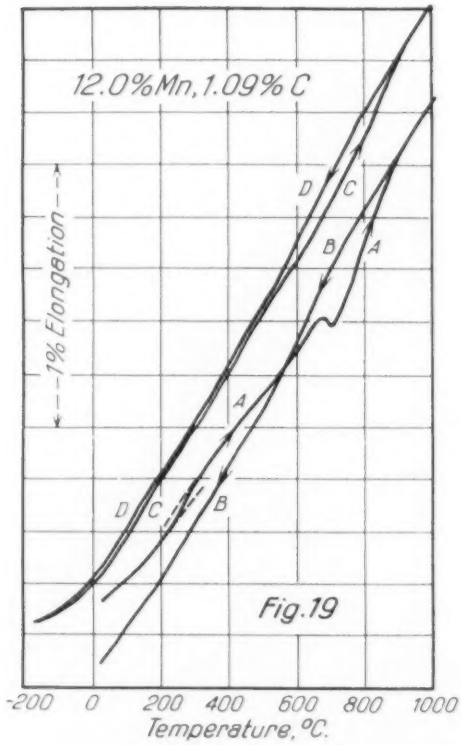
(3) No unambiguous evidence has been obtained to show that alpha can be formed from epsilon or epsilon from alpha.

If epsilon is stable and forms directly from gamma, the gamma-epsilon transformation differs from the gamma-martensite-alpha transformations in that the former give no intermediate unstable constituent, as does the latter.

The effect of carbon on the alpha-gamma and the epsilon-gamma transformations is to increase the hysteresis observed at moderate rates of heating and cooling. The presence of carbon decreases the amounts of both alpha and epsilon formed and about 0.50 per cent of carbon is sufficient to suppress the transformations.

Dilatometric Observations of Gamma Decomposition

While the formation of epsilon cannot be observed microscopically, it can be studied dilatometrically, because of the volume changes involved in its transformation. In comparison with the 0.03 per cent



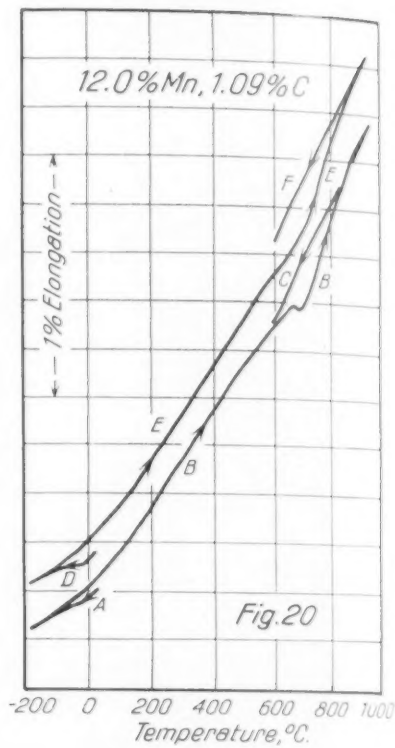


Fig. 19—12.0 per cent Manganese, 1.09 per cent Carbon. Homogenized (Five Hours at 1150 Degrees Cent. and Furnace-cooled). Cold-worked, Soaked Two Weeks at 550 Degrees Cent. Heating and Cooling Rate 10 Degrees Cent. per Minute.

Fig. 20—12.0 per cent Manganese, 1.09 per cent Carbon. Homogenized. Curve ABC after Soaking Two Weeks at 550 Degrees Cent. Curve DEF after a Six Hour Soak at 590 Degrees Cent.

carbon alloy, in the 0.24 per cent carbon alloy as forged, the amount of epsilon formed is less and the temperature at which it begins to form is lower (Figs. 15 and 16). The epsilon transformation is not observable in the 0.46 per cent alloy, when heated and cooled at 10 degrees Cent. a minute. Such observations as these indicate that gamma transforms to epsilon only when low in carbon. Carbon lowers the gamma to alpha transformation and reduces the amount of alpha formed at moderate rates of heating and cooling. With a carbon content greater than 0.80 per cent, dilatometric observations at heating and cooling rates of 10 degrees Cent. a minute show a loop due to carbon going into and coming out of solution. When carbides were precipitated by various methods, large amounts of epsilon were formed in the low carbon alloys but low temperature transformations were scarcely observable in the high carbon alloys.

For example, when the 0.46 per cent carbon alloy was cold worked and soaked for two weeks at 550 degrees Cent. (1020 de-

grees Fahr.), on cooling to room temperature, about thirty per cent of the alloy transformed to epsilon and some alpha was formed as well. (Fig. 17). The specimen was heated to 850 degrees Cent. but was not held long enough for much diffusion of carbon to occur and the amount of epsilon formed on cooling was decreased. Heating to 1000 degrees Cent. and cooling immediately permitted enough carbon migration so that on cooling very little epsilon appeared. With additional soaking as much as forty-five per cent of epsilon was formed on cooling. (Fig. 17 A).

The 0.82 per cent carbon alloy when cold-worked and soaked for two days at 550 degrees Cent. (1020 degrees Fahr.) formed only fifteen per cent epsilon and the 1.09 per cent alloy showed only the slightest indication of epsilon after cold working and soaking for two weeks at 550 degrees Cent. (Figs. 18 and 19). Slight amounts of alpha also were formed when these soaked alloys were cooled to a low enough temperature. (Fig. 20). The small amount of low temperature decomposition may be due to the following causes: (1) the conditions of time and temperature were not such as to bring about a sufficiently complete separation of carbon from the gamma phase, or (2) the manganese taken by the carbides left the gamma matrix too low in manganese to permit the formation of epsilon.

A specimen of the 1.57 per cent carbon alloy was examined by X-rays at room temperature after it had been cold-worked and soaked for two weeks at 550 degrees Cent. (1020 degrees Fahr.). It was found that almost all of the gamma phase had transformed to alpha and carbides.

Summary

The section of the ternary iron-manganese-carbon system has been determined at substantial equilibrium for pure alloys containing thirteen per cent manganese and varying carbon.

After the separation of carbides by cold working and soaking, the gamma remaining transformed principally to epsilon on cooling. The amount of gamma decomposed below the soaking temperatures decreased with increase in the carbon content.

ALLOYS OF IRON, MANGANESE AND CARBON—PART VIII

*Influence of Carbon on Ten Per Cent Manganese Alloys**

By John F. Eckel and V. N. Krivobok

Abstract

The work, as presented in this paper, deals with pure alloys containing iron, 10 per cent manganese, and carbon, the latter varying from 0.01 to 1.4 per cent. These alloys represent the 10 per cent manganese section of the iron-manganese-carbon ternary system investigated at Carnegie Institute of Technology, Pittsburgh.

The phase diagram, at substantial equilibrium was determined and is included in the paper. The phases present are gamma solid solution, alpha solid solution and carbides. The epsilon phase found in some alloys in small amounts is not included in the phase diagram. The methods used for the determination of boundary limits for various fields are described. In addition, the paper contains extra diagrams showing the influence of composition and previous heat treatment on the decomposition of gamma phase. No mechanical properties have as yet been determined, but the summary of variation in hardness brought about by different treatments is included.

Introduction

THE work presented in this paper comprises a part of the comprehensive study of high purity alloys of iron, manganese and carbon. The precautions taken to insure the purity of the materials used in this investigation have already been described.[1] A series of 10 per cent manganese alloys (with variable carbon content) was prepared from vacuum melted electrolytic iron and distilled manganese. They were melted in an induction furnace under purified argon

*This paper was condensed from a thesis submitted by John F. Eckel to the College of Engineering of the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science, Pittsburgh, June, 1932.

[1]F. M. Walters, Jr., "The Alloys of Iron, Manganese and Carbon—Part I. Preparation of the Alloys," Transactions, American Society for Steel Treating, Vol. XIX, 1932, p. 577.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. John F. Eckel is at present metallurgist with the Gulf Refining Co., Pittsburgh. Manuscript received June 6, 1932.

at atmospheric pressure. Such impurities as sulphur, phosphorus and silicon were present in amounts so small that they could not be estimated by ordinary standard methods.

The alloys were allowed to solidify in the furnace and upon cooling, the ingots were removed and forged into rods, roughly half an inch in diameter, a reduction of 90 to 95 per cent.

Table I

Ten Per Cent Manganese Alloys and Chemical Compositions

	Carbon Per cent			Manganese Per Cent			Homogenizing Treatment	
							Time	Temperature
Alloy	Top	Bottom	Average	Top	Bottom	Average	Hours	Degrees Cent.
A-41	0.015	0.015	0.015	10.30	10.44	10.4	10	1200
A-5	0.042	0.040	0.40	10.17	10.24	10.2		
A-31			0.29			10.2	10	1300
H-2	0.47	0.51	0.49	9.51	9.79	9.7	9	1270
A-38*	0.68	0.76	0.73	9.21	9.34	9.4	10	1240
A-39	1.26	1.25	1.25	10.45	10.43	10.4	10	1200
H-1	1.34	1.39	1.37	10.54	10.68	10.6	10	1200

*Only that part of the forged bar which came from the bottom of the ingot was used in the investigation.

Homogenizing Treatment

To render the forged alloys sufficiently homogeneous for precise determination of the various transformation temperatures, the forged alloys were held at temperatures near the solidus for about ten hours. To prevent the loss of carbon and manganese at the surface, the homogenizing treatment was carried out in purified helium at atmospheric pressure. The samples were cooled in the furnace to room temperature in about ten hours. After this treatment the surfaces of the bars were found to be completely free from oxidation (in fact quite bright) and microscopic examination revealed no decarburization.

Dilatation

In the determination of the 10 per cent manganese section of the ternary phase diagram, equilibrium was approached as nearly as possible. A preliminary study of the alloys by means of a simple dilatometer yielded interesting information in regard to the manner in which the alloys decomposed. In general, the observations were made at a heating and cooling rate of about 12 degrees Cent. a minute. During the course of the dilatometric investigation, transformational characteristics were observed in the ternary alloys, which were dif-

ferent from those observed in the binary alloys. Curves for the homogenized 0.29 per cent carbon alloys are similar to those obtained with the 0.015 per cent carbon alloy which have already been described in detail.[2] As should be expected, the temperature of the

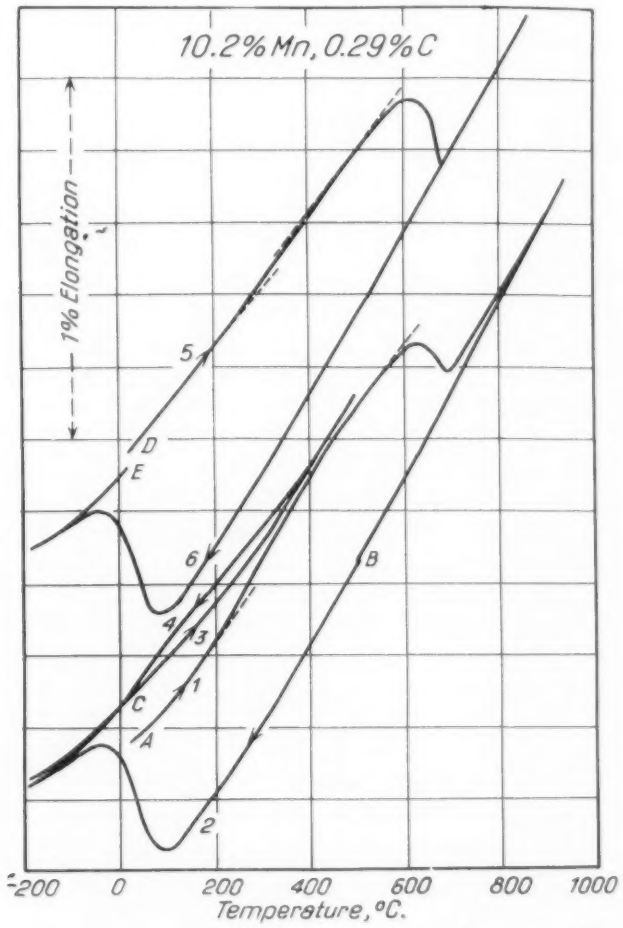


Fig. 1—Dilatation of a Homogenized Specimen of the 0.29 per cent Carbon Alloy.

gamma to alpha transformation range is lowered by the addition of carbon (cooling rate of 12 degrees Cent. per minute). Curves 5 and 6 in Fig. 1 show a typical heating and cooling cycle during which the gamma to alpha and alpha to gamma transformations occur. That some epsilon forms in 0.29 per cent carbon alloy is shown by the loop of curves 3 and 4. In curve 1 (first dilatometric run after

[2]F. M. Walters, Jr., and M. Gensamer, "Alloys of Iron-Manganese-Carbon—Part IV. A dilatometric Study of Iron-Manganese Binary Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. XIX, 1932, p. 607.

homogenizing) the expansion observed probably indicates further formation of alpha, accompanied by some epsilon to gamma transformation, the latter occurring over the same temperature range. Since about half of the gamma to alpha transformation takes place below room temperature, it is not surprising that incomplete decom-

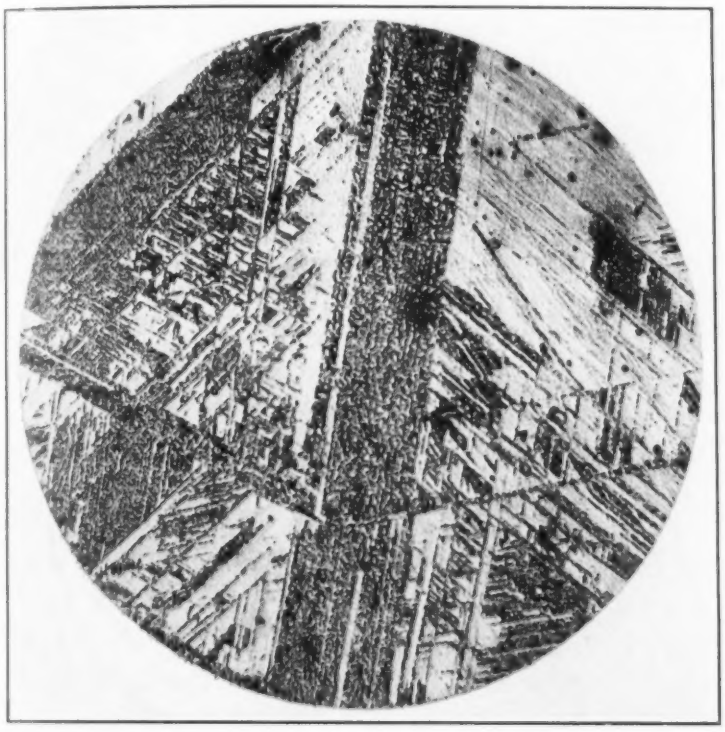


Fig. 2—Photomicrograph of a Homogenized Specimen of the 0.29 Per Cent Carbon Alloy. Note the Partial Decomposition of the Gamma Phase. Etched with 4 Per Cent Nital. × 250.

position of the gamma phase is observed in a specimen cooled only to room temperature. Widmanstatten patterns (Fig. 2) displaying incomplete decomposition are then observed unless decomposition is allowed to proceed very slowly. Structures of this type have been observed in the binary alloys containing 16 to 30 per cent manganese.[3]

At the usual rate of cooling, the beginning of the gamma to alpha transformation in the forged 0.49 per cent carbon alloy is depressed to about 25 degrees Cent., by the increase in carbon content. Consequently, samples of this alloy cooled to room temperature without previous separation of carbides show only incipient decomposition.

[3]V. N. Krivobok and Cyril Wells, "Alloys of Iron, Manganese and Carbon—Part V. Microscopic Studies of Binary Iron-Manganese Alloys."

After heating the same alloy for 16 hours at 550 degrees Cent. (1020 degrees Fahr.), sufficient separation of carbides took place to raise the gamma to alpha transformation, with a consequent formation of a loop similar to those of the low carbon alloys. Above the alpha to gamma transformation, a second smaller loop appears as the result of the re-solution of precipitated carbides.*

With a carbon content of 0.76 per cent, the start of the gamma to alpha transformation is lowered to about —90 degrees Cent. in the forged alloy. No discontinuities in the dilatometric curve suggestive of phase changes are observed when a specimen of this alloy is heated to 1000 degrees Cent. (1830 degrees Fahr.) and cooled to room temperature at the rate of 12 degrees Cent. per minute. However, if the specimen is held at 490 degrees Cent. (915 degrees Fahr.) for 16 hours, definite decomposition occurs, resulting in the formation of some alpha. After decomposition at 490 degrees Cent. (915 degrees Fahr.) for 16 hours, distinct decomposition occurs, and the formation of some alpha takes place on cooling. The gamma to alpha transformation observed on cooling after decomposition at 490 degrees Cent. occurred at a higher temperature than in the 0.49 per cent carbon alloy. Under the same conditions of heat treatment, this transformation in the 0.76 per cent carbon alloy might be expected to occur at a lower temperature than in the 0.49 per cent carbon alloy decomposed at 550 degrees Cent. (1020 degrees Fahr.). This type of behavior clearly demonstrates the change of solubility of carbides with temperature, and also the dependence of the transformation temperature of the residual gamma (in the hypereutectoid alloys) upon its carbon content.

Dilatometric curves typical of the higher carbon alloys (1.25 and 1.37 per cent carbon) are shown in Fig. 3. Curves 11 and 12 (beginning at J and ending at K) show the type of loop obtained when a sample is heated to 1000 degrees Cent. and air-quenched to retain carbon in solution in the gamma phase. The hysteresis of such a loop is the result of a definite expansion occurring as carbon is dissolved. When a specimen (in the air-quenched condition) is heated to 500 degrees Cent. and maintained at that temperature for some time (curve 13, K to L) a definite decomposition is observed: in this particular case, the decomposition consists mostly of the precipitation of

*Carbide precipitation is accompanied by a decrease in volume, in spite of the low density of cementite. X-ray measurements show that upon the precipitaton of carbides, the gamma lattice shrinks sufficiently to account for the observed volume change.

carbides and is indicated by a contraction. If heating is continued, an expansion may be observed which indicates the formation of pearlite. It is of particular interest to note that the decomposition recorded at "L" in Fig. 3, was apparently sufficient to permit the

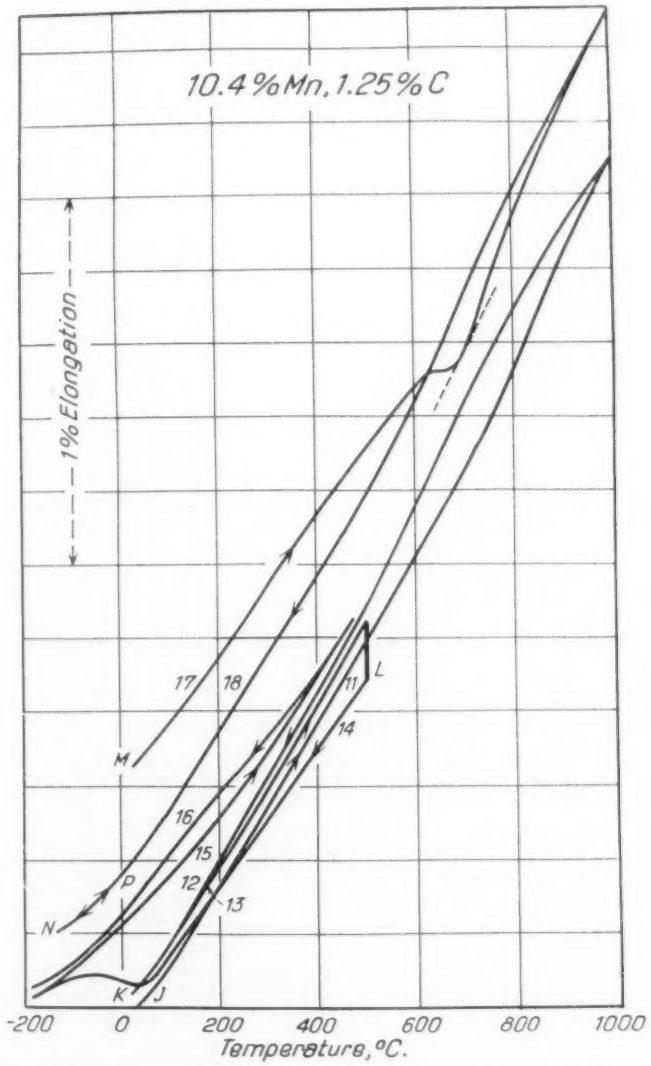


Fig. 3—Dilatation of a Homogenized Specimen of the 1.25 per cent Carbon Alloy.

occurrence of the gamma to alpha transformation, beginning at about 50 degrees Cent. The formation of some epsilon is shown by the typical loop of curves 15 and 16.

Curve 17, the sequel to curve 16, has been raised in the figure in such a way that M and P represent the same point. The alpha

to gamma transformation occurs just below 700 degrees Cent., and is partially masked by the solution of carbon in the newly formed gamma lattice. Above 700 degrees Cent., the usual carbon solubility loop is formed between curves 17 and 18.

"Spontaneous" Transformation of the Alloys as Forged

The temperature at which the gamma phase transforms to alpha depends upon the rate of cooling. The rate of 12 degrees Cent. a minute used in the dilatometric work is a convenient rate for making

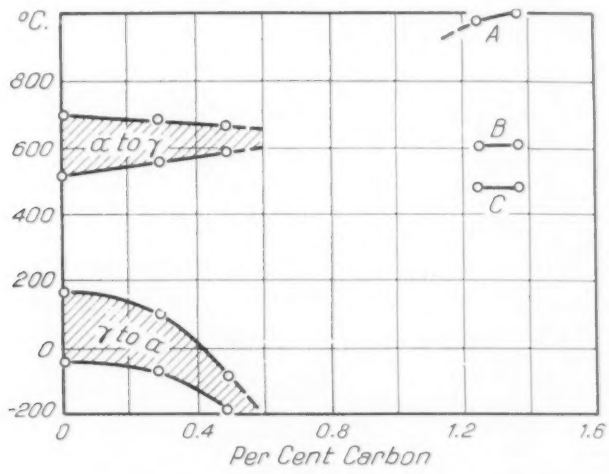


Fig. 4—"Spontaneous" Transformations in the Forged 10 per cent Manganese Alloys. Precipitation of Carbides was Observed Between B and C, and Solution of Carbides Between A and B.

observations and corresponds to a rapid "furnace cool." Transformations which occur at this rate of cooling are here termed "spontaneous."

The effect of carbon on the "spontaneous" formation of the alpha phase is given here for the alloys as forged and as homogenized and after holding near 500 degrees Cent. for several hours.

The effect of carbon on the "spontaneous" transformations in the 10 per cent alloys is shown in Fig. 4. With increasing carbon, the temperature at which gamma begins to transform to alpha* is lowered from 160 degrees Cent. for the 0.015 per cent carbon alloy to —80 degrees Cent. for the 0.76 per cent carbon alloy. On heating,

*Alloys under investigation also contained the epsilon phase, (hexagonal close-packed, denser than gamma), but its amount is so small that it must be considered as a secondary constituent.

the temperature at which the alpha to gamma transformation is completed[1] is lowered very slightly.

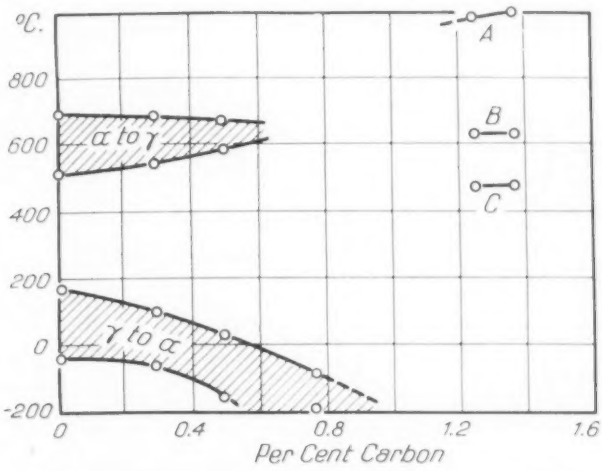


Fig. 5—"Spontaneous" Transformations of the Homogenized 10 per cent Manganese Alloys. Less Carbon is Required to Prevent the Decomposition of Gamma than with the Alloys as Forged. Precipitation of Carbides were Observed Between B and C, Solution of Carbides Between A and B.

It is apparent from the diagram in Fig. 4 that within a narrow range of composition gamma solid solution constitutes the only phase present at ordinary temperatures, even when a relatively slow rate of cooling is employed. This range of composition lies approximately between 0.60 per cent carbon and 1.0 per cent carbon. In alloys containing less than 0.60 per cent carbon the gamma phase partially decomposes to alpha at room temperature, while above 1 per cent carbon a new phase (carbides) appears. However, carbide precipitation may be prevented by an increased rate of cooling.

Spontaneous Transformations of the Homogenized Alloys

Because of the selective mode of freezing, iron-manganese-carbon alloys are afflicted, to a greater or less extent, with heterogeneity. When the composition of a sample of an alloy varies from point to point, the transformation temperatures are not characteristic of the

[1] "The temperature of the start of the Ar_3 ..... is the most significant characteristic of that change, is easily recognized and is practically independent of the rate of cooling. The end of the Ac_3 .... is the only temperature which can be easily and readily evaluated. Howard Scott. Transformational Characteristics of Iron-Manganese Alloys." American Institute of Mining and Metallurgical Engineers. Technical Publication 435, September, 1931.

average composition, but of those regions which are highest or lowest in the added elements.

Maintaining the alloys for several hours at temperatures near the solidus (to approach more uniform distribution of the elements) brought about those changes in the "spontaneous" transformations

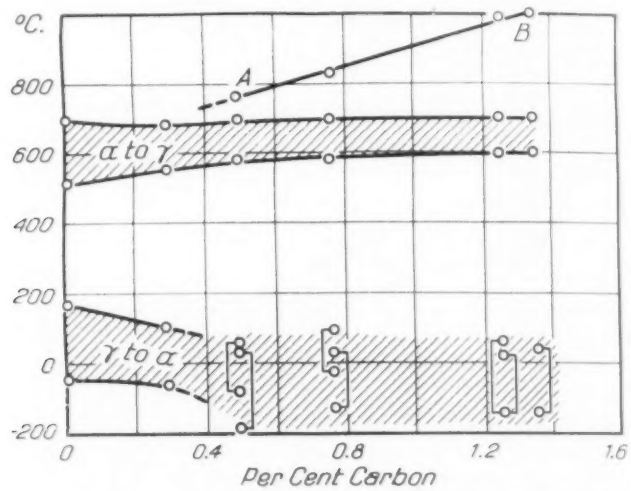


Fig. 6—"Spontaneous" Transformations of the Homogenized 10 per cent Manganese Alloys after Soaking the Hypereutectoid Alloys Near 500 Degrees Cent. "Spontaneous" Transformations are Shown in All of the Alloys. AB is Carbon Solubility Curve.

which might reasonably be anticipated (Fig. 5). The addition of increasing amounts of carbon lowers the temperature at which the gamma to alpha transformation begins more than in the case of the as forged alloys. For example, complete retention of the gamma phase at room temperature was observed at 0.40 per cent carbon as contrasted with 0.60 per cent carbon in "as forged" material. In alloys of higher carbon content decomposition of the gamma phase did not occur even at —190 degrees Cent. Dilatometrically only a slight difference was observed in the temperatures of complete carbide solubility in the alloys as forged and as homogenized. In the high carbon alloys no "spontaneous" transformations involving the alpha phase were observable, but at a heating and cooling rate of 12 degrees Cent. per minute, changes in length were picked up between 460 and 1000 degrees Cent. (Fig. 5) which were caused by the precipitation and solution of carbides. Alloys which had been air-cooled gave definite indications of carbide precipitation between 460 and 610 degrees Cent. (on heating). Above this temperature the carbides are re-dissolved.

"Spontaneous" Transformations after High Temperature Decomposition

When the alloys which do not undergo a gamma to alpha transformation at a cooling rate of 12 degrees Cent. per minute are held at a temperature near 500 degrees Cent. for several hours the gamma phase partially decomposes with the formation of primary carbides and pearlite.* Pearlite formation is, of course, indicative of partial change from gamma to alpha. Upon cooling, immediately following

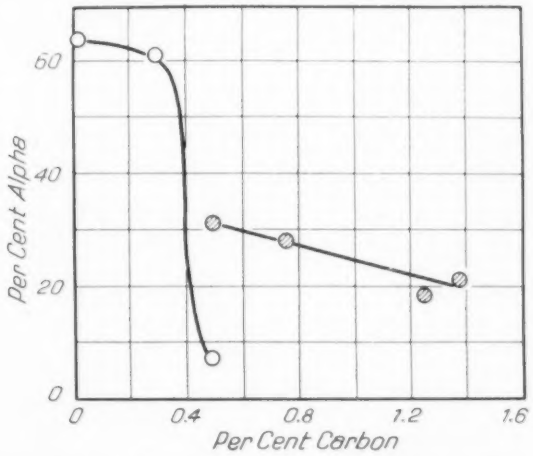


Fig. 7—Percentage of Alpha Formed by "Spontaneous Gamma to Alpha Transformations. Open Circles, without Previous Decomposition, Shaded Circles After Decomposition Near 500 Degrees Cent.

the soaking at 500 degrees Cent., further gamma to alpha transformation takes place within a certain temperature range, the limits of which depend upon the degree of decomposition. (See Fig. 6). Since in these alloys the carbides are known to contain as much as 22 per cent manganese,[5] carbide precipitation diminishes the manganese content of the gamma matrix and, consequently, the temperature of the gamma to alpha transformation should be raised. All hypereutectoid alloys investigated (with carbon as high as 1.37 per cent) gave the "spontaneous" gamma to alpha transformation after they had been soaked near 500 degrees Cent. On reheating, the highest temperature at which alpha is still present is independent of the carbon content of the alloys. (Fig. 6). In the same figure the curve

*In hypereutectoid alloys, i.e. in those containing carbon above 0.35 to 0.40 per cent.

[5]J. O. Arnold and A. A. Read, "Chemical and Mechanical Relations of Drawn Manganese and Carbon Alloys," *Journal*, Iron and Steel Institute, Vol. 38, 1910, p. 174-180.

AB shows the temperatures of the complete solution of carbon, as observed dilatometrically.

Amount of Alpha Formed in "Spontaneous" Transformations

The approximate percentage of alpha formed on cooling (the rate of which was 12 degrees Cent. per minute) is plotted in Fig. 7 as a function of the carbon content. The data were obtained for temperatures as low as —192 degrees Cent. and are for the homogenized alloys (a) with and (b) without decomposition near 500 degrees Cent.

The 0.015 per cent carbon alloy is only about 65 per cent alpha, and of the remainder about ten per cent is epsilon. As the temperature is raised from that of liquid nitrogen a little alpha is formed up to 400 degrees Cent., but about twenty per cent of the alloy persists as gamma at all temperatures of the heating and cooling cycle.

The amount of alpha appearing in the 0.29 per cent carbon alloy, is nearly the same as in the 0.015 per cent carbon alloy, but this amount rapidly diminishes as the carbon is increased to about 0.50 per cent (Fig. 7). Incidentally, it may be of interest to mention that the eutectoid point in the 10 per cent manganese alloys lies between 0.30 and 0.40 per cent carbon.

After soaking the 0.49 per cent carbon alloy near 500 degrees Cent., about 30 per cent of the sample transforms to alpha on cooling. For the higher carbon alloys the amount of alpha formed is slightly less. Of course, it is to be understood that the amount of alpha formed also depends upon the time of soaking, although after a few hours the reaction slows down very considerably.

Determination of Phase Diagram

So far the discussion has dealt with the constitution of the 10 per cent manganese alloys as determined by heating and cooling rates too rapid to approach equilibrium conditions. By maintaining the alloys near 500 degrees Cent. an indication is obtained as to the type of reactions which take place in the higher carbon alloys as they approach equilibrium. When equilibrium is substantially attained the phase limits can be determined quite accurately. The method selected for the purpose was that of microscopic examination of samples which had been heated in vacuo to several temperatures and held sufficiently long to approach equilibrium.

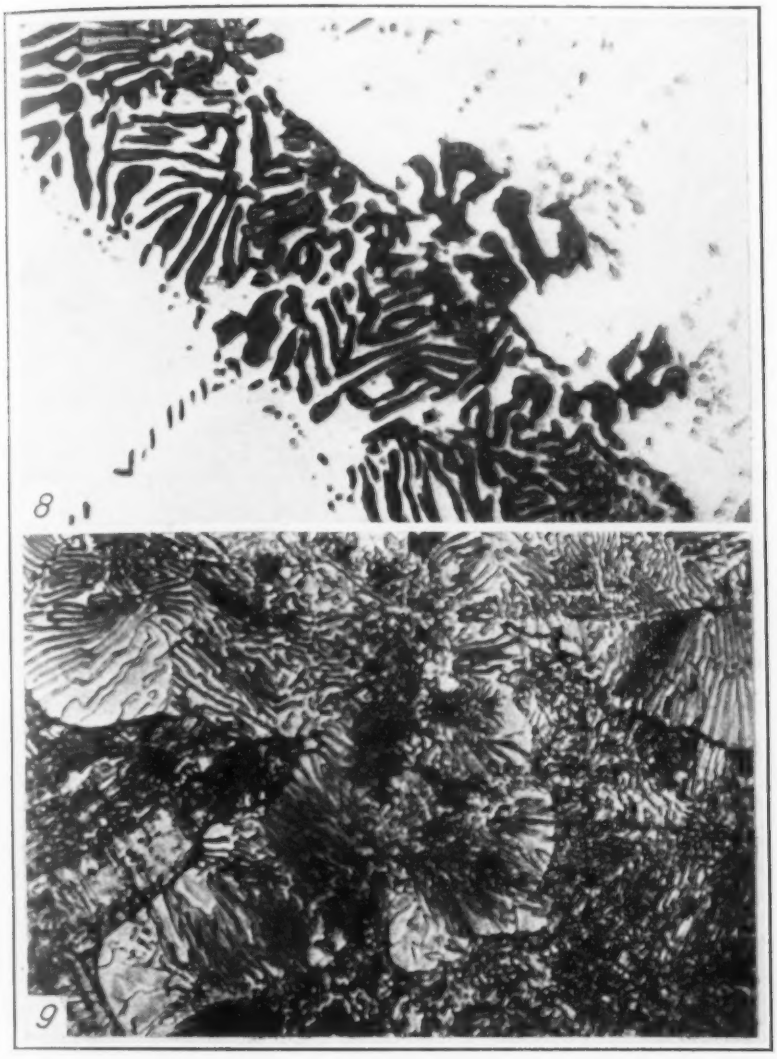


Fig. 8—Photomicrograph of a Homogenized Specimen of the 0.76 Per Cent Carbon Alloy, Slowly Cooled from 1030 to 700 Degrees Cent., Quenched, Reduced 5 Per Cent in Length by a Static Load, Heated One Week at 650 Degrees Cent. in Vacuo and Quenched. Note the Pearlitic Structure. Etched with Sodium Picrate. × 2000.

Fig. 9—Photomicrograph of the 0.49 Per Cent Carbon Alloy, Heated One Week at 560 Degrees Cent. and Furnace-Cooled, Showing a Pearlitic Structure and Decomposed Gamma. Etched with 4 Per Cent Nital. × 2000.

Determination of the Temperature Limits of the Alpha Phase

In determining the stability limit of the alpha phase, the alloys were given special treatment to decrease the time required to approach equilibrium at the various soaking temperatures. Homogenized specimens of the hypereutectoid alloys were held at 1030 degrees Cent.

long enough for the carbides to go completely into solution, then slowly cooled to 700 degrees Cent. to form pro-eutectoid carbides, rapidly quenched, and, finally, given a five per cent reduction in length by means of a static load. The purpose of the cold work was to introduce some disorganized material which, upon recrystallization within any range, would revert to the phase (or phases) characteristic of that range. Thus, the highest temperature at which alpha exists in the hypereutectoid alloys, would be determined by observing whether or not pearlite was present after a long soak at various temperatures. If the temperature were in the stability range for alpha iron, pearlite would be formed but, if the temperature were above this range the disorganized material would revert back to austenite (gamma iron). (Typical photomicrographs are shown in Figs. 8 and 9).

At the soaking temperatures of 625, 650, 675 and 700 degrees Cent., it was possible to protect the specimens from oxidation by sealing them in evacuated pyrex containers. The temperature control was within plus or minus 5 degrees Cent. The temperature of the specimens was observed by means of a chromel-alumel thermocouple attached to a piece of stainless steel, which was of the same mass as the samples and, like them, enclosed in another pyrex container. Care was taken in the manipulation of the furnace to bring the specimens to temperature in ten minutes. Although all heat treatments were carried out in vacuo or in helium, the additional precaution was taken of grinding off the surface before microscopic examination.

With the hypoeutectoid alloys a different procedure had to be adopted. Both the 0.015 and 0.29 per cent carbon alloys start to transform to alpha above 100 degrees Cent. and display a Widmanstatten pattern when cooled to room temperature. When these two alloys were heated to 800 degrees Cent. (to insure that they were entirely in the gamma state), cooled to 135 degrees Cent. and held at this temperature for 21 hours, the Widmanstatten lamellae agglomerated. (Fig. 10). Specimens so treated were held for one week in vacuo at 625, 650, 675, and 700 degrees Cent., and quenched. If the soaking temperature was above the stable alpha range, the agglomerated structure disappeared and was replaced by the Widmanstatten pattern indicative of directional decomposition. (Fig. 11). After one week at 625 degrees Cent. parts of the specimen with 0.29 per cent carbon showed this directional decomposition, therefore

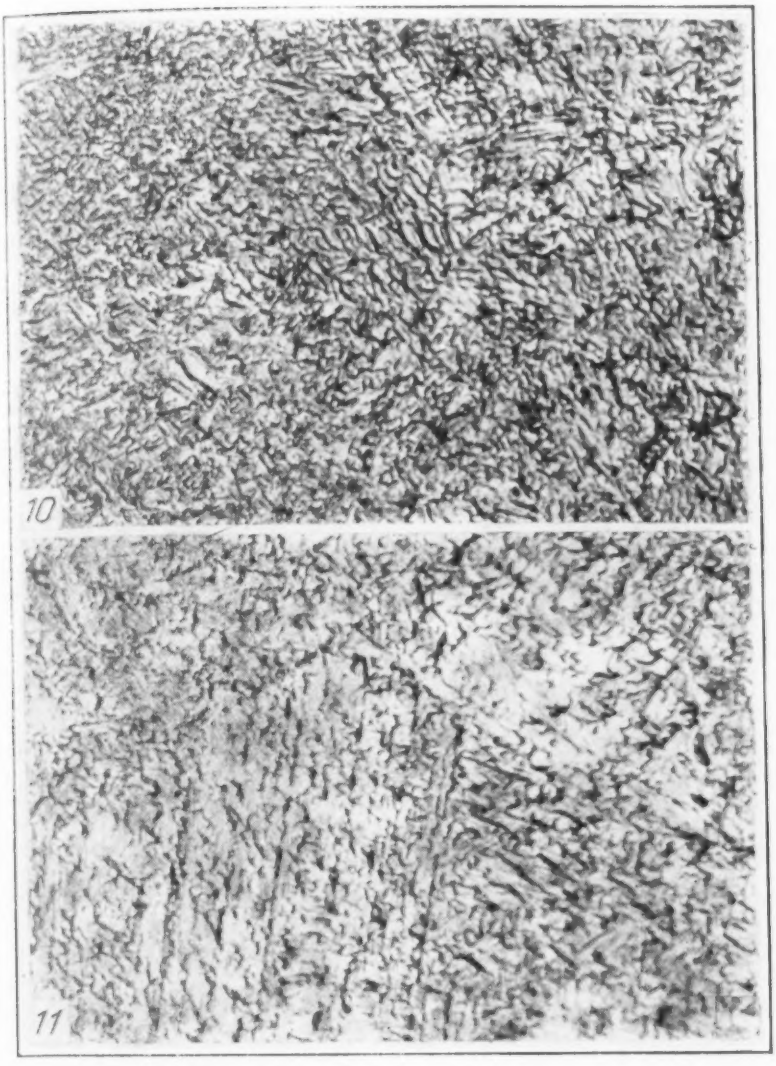


Fig. 10—Photomicrograph of a Homogenized Specimen of the 0.015 Per Cent Carbon Alloy, Heated to 800 Degrees Cent., Cooled to 135 Degrees Cent., Held for 21 Hours, Soaked One Week at 625 Degrees Cent. in Vacuo and Quenched. Note the Agglomerated Type of Structure. Etched with Nital. × 2000.

Fig. 11—Photomicrograph of a Homogenized Specimen of the 0.015 Per Cent Carbon Alloy Heated to 800 Degrees Cent., Cooled to 135 Degrees Cent., Held 21 Hours, Soaked One Week at 700 Degrees Cent. in Vacuo and Quenched. Directional Decomposition of Large Gamma Grains Indicates that the Specimen Was in the Gamma Region. Etched with 4 Per Cent Nital. × 2000.

indicating that this temperature is within the two phase region. The appearance of the structure of the 0.015 per cent carbon alloy after similar treatment did not change materially, although there was some evidence of recrystallization. While more than half the alpha present at room temperature has transformed to gamma when the temperature

is raised to 625 degrees Cent., grain growth at this temperature is very slow (in the low carbon alloys) and considerable time would be required to grow grains large enough to differentiate the two phases.

The agglomerated 0.015 per cent carbon specimen held at 675 degrees Cent. for one week showed a Widmanstatten pattern thus

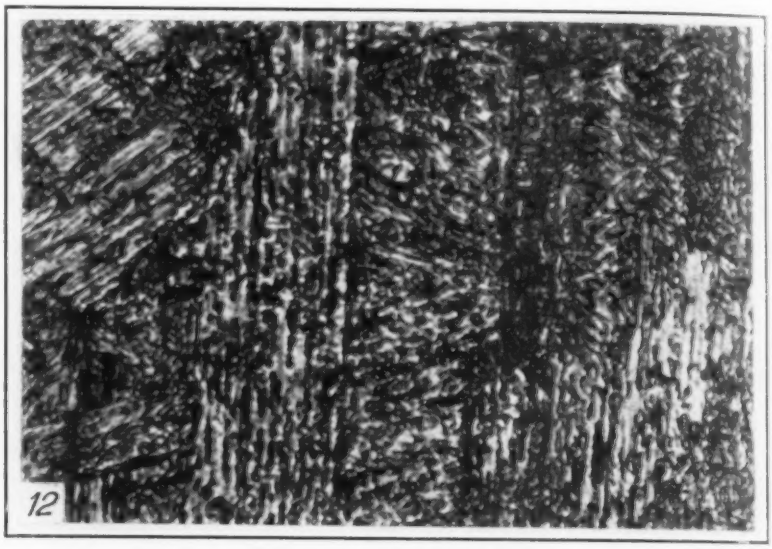


Fig. 12—Photomicrograph of a Homogenized Specimen of the 0.29 Per Cent Carbon Alloy Heated to 800 Degrees Cent., Cooled to 135 Degrees Cent., Held 21 Hours, Heated One Week in Vacuo at 650 Degrees Cent. and Quenched. Directional Decomposition Indicates that the Limit of the Alpha Phase has been Passed. Etched with 4 Per Cent Nital. × 2000.

agreeing with the dilatometric observations that the alpha to gamma transformation is complete at 660 degrees Cent. At 650 degrees Cent. the agglomerated structure of the 0.29 per cent carbon alloy disappeared. (Fig. 12).

Table II
Upper Temperature Limit of the Alpha Phase

Alloy	Manganese Per cent	Carbon Per cent	Temperature in Degrees C	
			Alpha present	Alpha absent
A-41	10.4	0.015	650	675
A-31	10.2	0.29	625	650
H-2	9.7	0.49	650	675
A-38	9.4	0.76	675	700
A-39	10.4	1.25	675	700
H-1	10.6	1.37	675	700

Determination of the Temperature Limits of the Carbide Phase

A number of experiments were conducted for the purpose of determining the solubility of carbon in the gamma phase of 10 per

cent manganese alloy, i.e., the boundary temperatures for the carbide phase. These experiments consisted of quenching the alloys from successively higher temperatures and observing that at which carbides disappeared. The specimens were heated in a vacuum furnace controlled to within plus or minus 5 degrees Cent.

The length of time of heating at each temperature was about two hours at the end of which, the specimen was quickly quenched in water. Temperature intervals of 25 degrees Cent. were selected so that if carbides were found, for example, at 900 degrees Cent., and not at 925 degrees Cent. the solubility point was midway. The specimens were polished, properly etched, and examined at high power for the last traces of carbides; where no carbides were observed on the first examination, the specimens were cut in two and the inner surfaces examined.

The "as forged" specimens were heated by successive steps until carbides had disappeared, thus giving an opportunity for some carbon to dissolve at each temperature. The same procedure was carried out on the homogenized alloys. In addition, other specimens of the homogenized alloys were heated first to a high temperature, quenched (so that all of the carbon remained in solution) and then held one week at 550 degrees Cent. to reprecipitate the carbides. These homogenized specimens were cut in two pieces, one of which was heated to the first temperature where the disappearance of carbides had been observed, quenched and examined. In case no carbides were observed on the outer surfaces, the specimens were again cut and the inner surfaces examined.

The experimental procedure had to be somewhat altered for the hypoeutectoid alloys. In these alloys the separation of carbides into a normal pearlite structure must be preceded by the rejection of some of the alpha phase. The persistence of the Widmanstatten pattern in the 0.29 per cent carbon alloy even when it is quenched from temperatures well in the gamma region excludes the use of the method adopted for higher carbon alloys, and another procedure had to be adopted. For example, a specimen of the homogenized 0.29 per cent carbon alloy was heated to 900 degrees Cent., squeezed in a vise and severely hammered while the sample was cooling to a black heat; then the specimen was placed in a furnace at 500 degrees Cent. After two hours at 500 degrees Cent. the specimen was quenched in water, polished and examined. The usual ten second

etch in hot sodium picrate revealed small patches of carbide, largely in troostitic formations along the grain boundaries.

The specimen of the 0.29 per cent carbon alloy containing the troostitic constituent was then cut in smaller pieces and heated to successively higher temperatures. Traces of the carbides were ob-

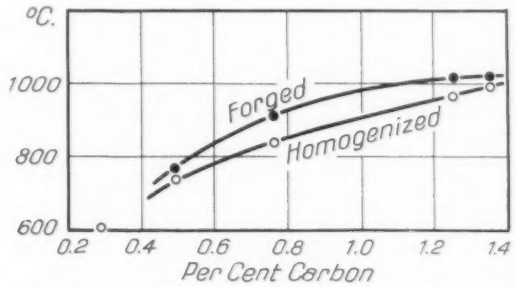


Fig. 13—Curves Showing the Solubility of Carbon in the Gamma Phase.

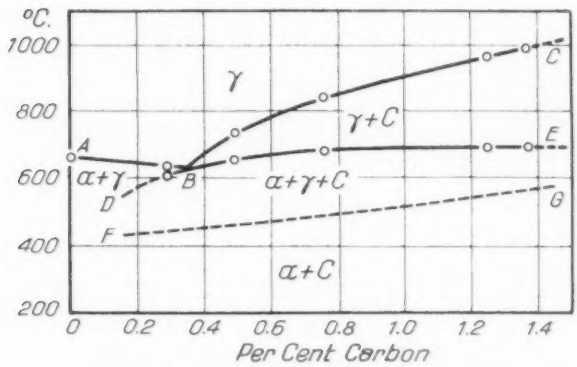


Fig. 14—Constitution of the 10 per cent Manganese Alloys at Substantial Equilibrium Conditions.

served at 600 degrees Cent., but these had completely disappeared at 625 degrees Cent. From these data, the solubility temperature of carbon in this alloy was taken to be between 600 and 625 degrees Cent.

The solubility of carbon has been plotted in Fig. 13. It is of particular interest to note the lower temperatures at which the carbides went into solution in the homogenized alloys.

The Ten Per Cent Manganese Section of the Ternary Iron-Manganese-Carbon System

The results of these determinations are plotted in Fig. 14, which shows the phases and their temperature limits in the 10 per cent

manganese alloys. Curve BC is the dividing line between the gamma and gamma plus carbide regions and is the solubility curve for carbon in the gamma phase; curve BD is also a carbon solubility curve.

Curve ABE represents the highest temperature at which alpha may exist as a stable phase. It is of particular interest to note the

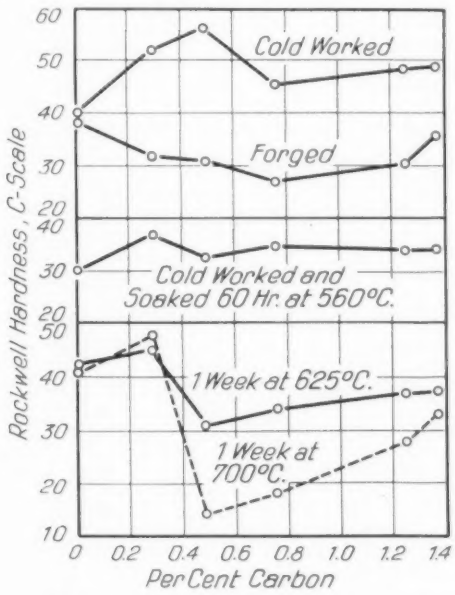


Fig. 15—Curves Showing the Hardness of the 10 per cent Manganese Alloys after Different Treatments.

gradual rising of curve BE with increasing carbon content, caused by the precipitation of manganese-rich pro-eutectoid carbides. Curve FG, representing the lower limit of the gamma phase, has not been determined because of the experimental difficulties, namely, the extremely long time required to establish even approximate equilibrium.

In considering this diagram, it should be borne in mind that it is not a binary diagram and that the curves are traces of surfaces within the ternary iron-manganese-carbon system. Such a diagram gives no indication of the relative amounts of phases present nor any idea of their composition. Curve BE, is, in reality, not in the 10 per cent manganese plane but is a projection of the eutectoid line on the 10 per cent manganese plane. Likewise, curve BD may be displaced from the 10 per cent manganese plane, the amount of this displacement being dependent upon the composition of the alpha phase separating. Curves AB and BE are true representations of the 10 per cent

manganese plane since they form part of the boundaries of a single phase region.

The Influence of Carbon on the Hardness of the Ten Per Cent Manganese Alloys

Hardness measurements were made on the alloys after various treatments. The particular heat treatments given were selected because of their bearing on the transformational characteristics of the alloys, and not to obtain maximum hardness. In making the observations the samples were cut in two and the hardness numbers shown in Fig. 19 are for the center of a half inch specimen.

The alloys as forged were cold-worked by giving a twenty per cent reduction with an air hammer. That the hardness of the 0.015 per cent carbon alloy was not increased by cold work is due to the fact that at room temperature the decomposition of the gamma phase is nearly complete and the structure is very fine grained.

Soaking these cold-worked samples for 60 hours at 560 degrees Cent. reduced the hardness to that of the alloys as forged.

The two lower curves of Fig. 15 give the hardness of the specimens used in the determination of the upper limit of the alpha phase. (The 0.015 and 0.29 per cent carbon alloys were not agglomerated specimens but others which had received the same treatment before soaking as the hypereutectoid specimens). At 700 degrees Cent., the phases present in the hypereutectoid alloys are gamma and carbides and on quenching the gamma is retained. On the other hand, at this temperature the hypoeutectoid alloys are entirely gamma and low in carbon so that on quenching a fine-grained structure results. The hypereutectoid alloys are composed of pearlite, primary carbides and gamma, while the hypoeutectoid alloys are composed of alpha and gamma.

RATES OF SCALE FORMATION ON IRON AND A FEW OF ITS ALLOYS

By K. Heindlhofer and B. M. Larsen

Abstract

Scaling is considered to be as a diffusion process. The simple case of a plane bounded pure metal capable of forming more than one oxide, hence more than one scale layer, is treated mathematically. It is shown that the thickness of each layer, hence the thickness of the whole scale increases as the square root of time and increases rapidly with rising temperature, according to an exponential relation. These simple relations are not strictly valid for alloys or for sharply curved surfaces such as wires. These conclusions are confirmed for pure iron and pure copper and a few iron alloys by experiments using relatively long periods of exposure and continuous weighing of the sample during the scaling period. Scaling of iron in water vapor and CO_2 proceeds at rates not only very different from those in air or oxygen, provided sufficient time is allowed for the attainment of steady state condition. The scaling of a few resistant alloys is studied.

THE purpose of the authors in this paper is, at the risk of appearing to repeat ideas already in the literature, to present a general picture of the process of scaling of a metal, and to emphasize the role played by diffusion through the actual scale layer. For a given type of scale, this phase of the process is substantially regular and predictable; and this general regularity aids us in disentangling the effects of the various factors which may be involved in practice. The early rate of scaling of a metal surface is more important practically in many cases, for instance in relation to heat treating operations; but this early rate is not always in fact reproducible as it is influenced by complex factors such as the character of the initial surface and the composition of the gas layer in immediate contact with the scaling surface, this in turn being determined by the composition of the gas and by its rate of flow past the surface. These influences, which may be hard to duplicate, decrease in relative importance as the scale

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grows, until finally the rate of scaling is limited chiefly by the rate of counter-diffusion of metal and corroding gas through the scale.

The data given are for iron and some of its alloys, but the main ideas are applicable to the rate of scaling of any metallic surface. The method of measuring scaling rates leads to fairly accurate and complete values of the rate constants for pure iron; the use of long-time experiments with frequent measurements has shown up certain irregularities in the scale growth on pure iron and certain of its alloys which are not so evident under other experimental conditions.

There are in the literature numerous data on the rate of scale formation on iron and other metals at various temperatures and in various atmospheres; but until recently little attempt was made to treat the problem in a fundamental way. Two papers by Pilling and Bedworth[1, 2] first introduced order into the study of the scaling process. Recognizing the fact that the growth of a scale layer depends on diffusion, they derived a quantitative relationship between elapsed time and thickening of scale at constant temperature, namely that the amount of scale varies as the square root of time. Their method of derivation of this relation seems to be based on premises not all of which are valid, yet the result is correct, and is in good agreement with their experimental data on the rate of oxidation of copper, nickel, iron, and the copper-nickel alloys between the limits of 0-35 per cent nickel and 80-100 per cent nickel. Moreover they observed that for a given period of scaling, the amount of corroding agent absorbed (or the increase in weight, W) by the specimen varies as a power of the absolute temperature (T), that is

$$W = kT^n$$

Dunn,[3] studying more particularly the variation in scaling rate with temperature, agreed that Pilling and Bedworth's results follow rather closely the relationship $W = kT^n$, but concluded that this correlation is not significant since the formula is purely empirical. He derived a formula of the form

[1] N. B. Pilling and R. E. Bedworth, "The Oxidation of Metals at High Temperatures," *Journal*, Institute of Metals, Vol. 29, 1923, p. 529-591.

[2] N. B. Pilling and R. E. Bedworth, "The Oxidation of Copper-Nickel Alloys at High Temperatures," *Industrial and Engineering Chemistry*, Vol. 17, 1925, p. 372-376.

[3] J. S. Dunn, "The High Temperature Oxidation of Metals," *Proceedings of Royal Society*, Vol. III A, 1926, p. 203-209.

$$W = ke^{-\frac{Q}{RT}} \qquad \text{or} \qquad \log W = a + \frac{b}{T}$$

whose validity he confirmed by plotting the experimental data for several brasses and a few pure metals in terms of low W against 1/T and finding that these plots are very close to straight lines.

Von Schwarze[4] studied the scaling of the iron-aluminum-chromium alloys and found two different types of scale. At an aluminum content in excess of around 11 to 14 per cent the scale is white and offers an effective protection against continued scaling even at high temperatures such as 1200 degrees Cent. (2190 degrees Fahr.). The scale formed on alloys containing less than about 7 per cent aluminum is the ordinary black scale formed on pure iron and has little protective effect. There exists an intermediate range at aluminum contents of around 7 to 11 per cent on which a white scale forms with black warts, originating perhaps at defects in the white layer. Our observations are substantially in agreement with these results as illustrated by the scaled specimens shown in Fig. 9. The thin black scale formed on the high chromium alloys was effective in preventing rapid scaling but not quite to the same degree as the white scale on the aluminum-rich alloys.

Mechanism of Scale Formation on Iron

The mechanism of scale formation may be explained on the basis of a series of investigations by Pfeil[5] on the scaling of iron and certain alloy steels. From the data in the literature[6, 7] we know that the oxygen pressure of Fe_2O_3 is, at all temperatures below about 1325 degrees Cent. (2420 degrees Fahr.), less than that of the atmosphere, so that iron heated with an excess of air or with any oxygen-air mixture should at any temperature below this limit ultimately form an Fe_2O_3 layer on the outside of the scale; (with higher tem-

[4]Hjalmar Von Schwarze, "Beitrag zur Kenntnis der Schützwirkung der beim Zundern auf Stahl gebildeten Oxydschichten," Mitteilungen aus dem Forschungs-Institut der Vereinigte Stahlwerke A.G., Dortmund, Vol. 2, 1932, p. 263-277.

[5]L. B. Pfeil, "The Oxidation of Iron and Steel at High Temperatures," *Journal*, Iron and Steel Institute, Vol. 119, No. 1, 1929, p. 501-560.
L. B. Pfeil, "The Constitution of Scale," *Journal*, Iron and Steel Institute, Vol. 123, No. 1, 1931, p. 237-258.

[6]R. B. Sosman and J. C. Hostetter, "The Oxides of Iron. Solid Solution in the Systems Fe_2O_3—Fe_3O_4," *Journal*, American Chemical Society, Vol. 38, 1916, p. 807-833.

[7]Magnus Tigerschiöld, "Jarnets Oxidei fran termodynamisk Synpunkt," *Jernkontorets Annaler*, 1923, p. 67-105.

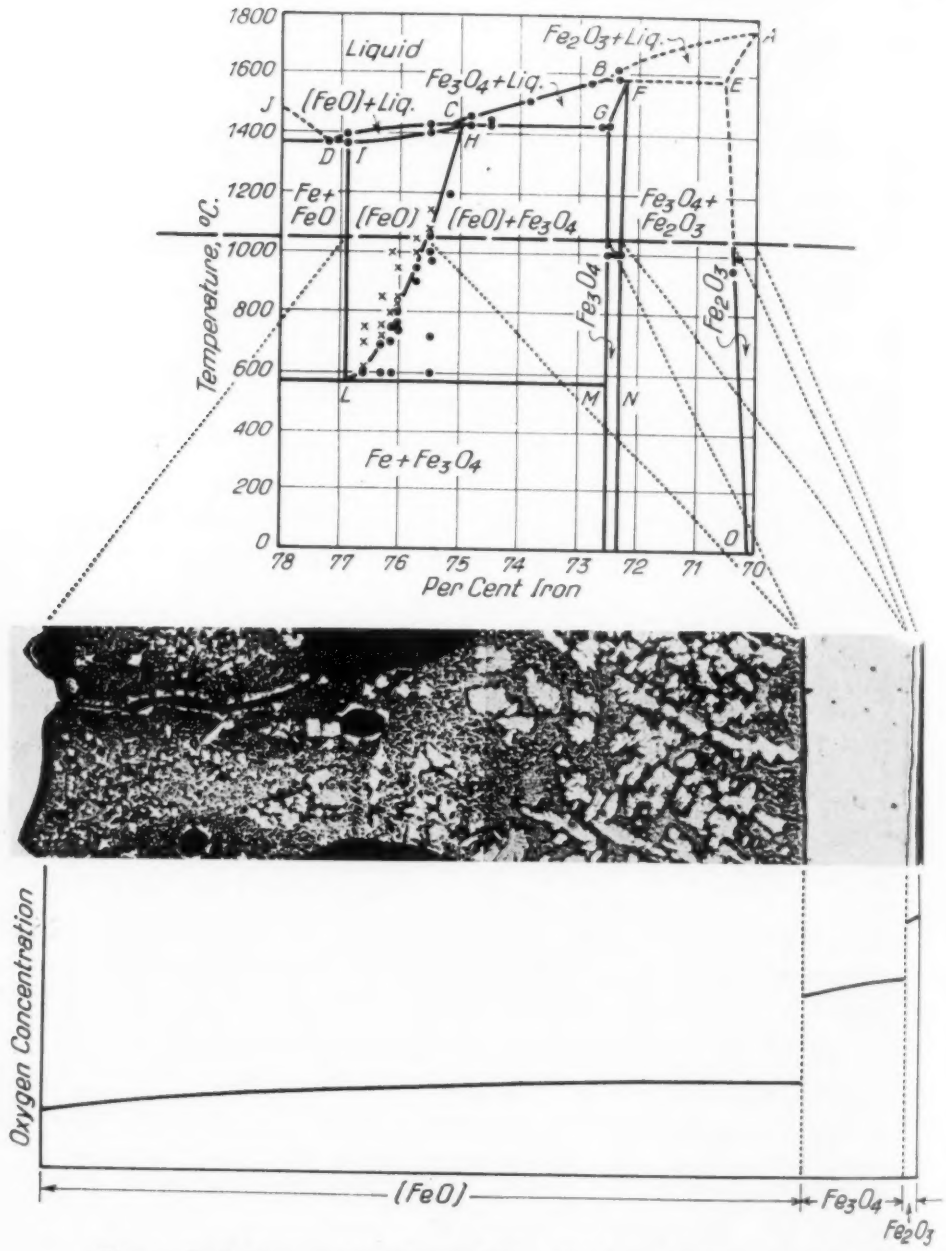


Fig. 1—Fe-O Diagram According to Pfeil. The Lower Curves Represent Qualitatively the Course of Decreasing Oxygen Content Between Outside and Inside of the Scale Shown in the Photograph.

peratures or lower oxygen pressures in the gas phase, the outside layer should approach Fe_3O_4). With Fe_2O_3 as the outside layer, the whole scale should then contain all the homogeneous phase mixtures possible in the iron-oxygen system between Fe_2O_3 and pure iron saturated with oxygen. This is illustrated by Fig. 1 which repro-

duces part of the Fe-O diagram according to Pfeil. Mathewson, Spire and Milligan[8] and Benedicks and Löfquist[9] have given Fe-O diagrams which differ from each other and from that of Pfeil, but chiefly in the liquidus and solidus lines at higher temperatures; we are here only interested in the series of solid solutions formed at temperatures in the range 600 to 1200 degrees Cent. (1110-2190 degrees Fahr.) for which these diagrams are in fair agreement. Moreover, the latest determinations of the boundaries of the wüstite (FeO) field by Jette and Foote[10] and by Vogel and Martin[11] are in close agreement with the data by Pfeil.

Below the equilibrium diagram of Fig. 1 is placed a photomicrograph of a section through the scale layer formed on pure iron at about 1050 degrees Cent. (1925 degrees Fahr.); it shows three distinct layers—a thin Fe_2O_3 skin on the right, then a layer of Fe_3O_4, and a much thicker layer of FeO in which a decreasing amount of dissolved Fe_3O_4 has separated in cooling as we move toward the extreme left, where the scale was originally in contact with the metal. Since the scale, formed as it is by a diffusion process, can contain only those mixtures of iron and oxygen which form homogeneous single-phase solutions at the scaling temperature (1050 degrees Cent. in this example) the composition at the several boundaries in the scale should correspond with those represented by the intersection of a horizontal at 1050 degrees Cent. with the several lines of the FeO diagram. The curves given below in Fig. 1 then represent qualitatively the course of decreasing oxygen content between outside and inside of the scale. Since the scale on pure iron (or carbon steel) contains nothing but iron and oxygen, the iron content rises in proportion to the drop in oxygen content. The outside scale surface should be pure Fe_2O_3, containing 69.9 per cent iron, which can dissolve Fe_3O_4 (or extra iron atoms, which amounts to the same thing) up to about 70.4 per cent iron. There is, at the Fe_2O_3-Fe_3O_4 boundary, a sharp rise in iron content to about 72.3 per cent iron;

[8]C. H. Mathewson, E. Spire and W. E. Milligan, "Evolution of the Iron-Oxygen Constitutional Diagram," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1931, p. 66-88.

[9]C. Benedicks and H. Löfquist, "Uber das System Eisen-Sauerstoff," *Zeit. Ver. Deutsche Ingen.*, Vol. 71, 1927, p. 1576-7.

[10]E. R. Jette and F. Foote, "A Study of the Homogeneity Limits of Wöstite (FeO) by X-ray Methods," American Institute of Mining and Metallurgical Engineers Preprint, Feb., 1933, 9 pages.

[11]R. Vogel and E. Martin, "Das System Eisenoxydul-Eisenoxyduloxyd," *Archiv. fur Eisenhüttenwesen*, Vol. 6, 1932, p. 109-111.

a gradual rise through the Fe_3O_4 layer to around 72.6 per cent iron; another sudden rise at the Fe_3O_4-FeO boundary to 75.6 per cent iron which represents FeO saturated with oxygen; finally a gradual rise to 76.9 per cent iron which is the composition of FeO, containing a little extra oxygen in solution, that is in equilibrium with iron at 1050 degrees Cent. This inner FeO layer consists of one phase while at the temperature of scaling, but on cooling the solubility of the excess oxygen decreases with the consequent separation of crystals of magnetite which constitute the bright areas in this layer in the picture of Fig. 1.

Now, imagine a surface of iron exposed instantly to air at, say, 1050 degrees Cent. (1925 degrees Fahr.). The first small amount of oxygen combining with the iron dissolves in the surface layer, but almost immediately a layer of FeO forms which grows by taking up more oxygen at its outside, and iron at its inside, surface. As this FeO layer grows thicker, oxygen diffuses in more slowly from the surface in contact with the atmosphere, and the oxygen concentration at the surface rises to the saturation value for oxygen in FeO. A layer of Fe_3O_4 then begins to form, which (always assuming that excess oxygen at a pressure above that of the dissociation pressure of Fe_2O_3 is supplied to the surface) becomes saturated with oxygen at its outside surface, where it oxidizes further to form a skin of Fe_2O_3. As soon as this outer skin has absorbed oxygen up to saturation the complete series of possible scale layers is formed and from this time on the *boundary conditions* in the scale are practically fixed at 69.9 per cent iron at the outside, and about 76.9 per cent iron at the inside, surface of the scale.

This point is important, since in order to apply a mathematical treatment to scale growth proceeding by diffusion, it is necessary to define fixed boundary conditions in order to be able to integrate the differential equations involved. In fixing the boundary conditions, it is also necessary to distinguish between the diffusion process in the gas phase and that in the scale layer. In air, the absorption of oxygen into the scale raises the nitrogen content in the immediately adjacent gas film so that oxygen must diffuse through nitrogen to reach the scale surface. When the scale is very thin, and the rate of absorption of oxygen comparatively rapid, this rate of effective oxygen supply by gaseous diffusion may be a limiting factor in the whole process. Whenever this is true, the rate of scale growth is obviously dependent not only on the properties of, and conditions in,

the scale itself (i.e., diffusion constant, oxygen gradient and temperature) but also upon a rate of gaseous diffusion.

For example, with a large fresh surface of a fairly fast scaling metal such as iron at 1000-1200 degrees Cent. (1830-2190 degrees Fahr.) it would be almost impossible to blow air past the surface fast enough to give an oxygen supply in excess of the amount which the initial thin scale layer is capable of absorbing. At a later period, however, when the scale has grown relatively thick, even the normal diffusion in still air might be sufficient to supply oxygen to the surface faster than it can diffuse through the thick scale. With a pure oxygen atmosphere, this limitation due to gas diffusion should not exist. Moreover the rate of scale formation should be just as high as in a pure oxygen atmosphere if oxygen is supplied rapidly enough by fast circulation of air or of any mixture of oxygen plus inert gas with an oxygen pressure above that of Fe_2O_3.

Murphy, Wood and Jominy[12] give some data showing how the rate of scaling increases with the rate of gas flow past the oxidizing surface up to a certain maximum, beyond which a further increase in rate of flow has no effect. This is quite reasonable, but such numerical data have little general value, since the minimum rate of gas flow necessary to cause this maximum rate of scaling varies not only with the gas composition and the kind of metal being oxidized but also with the temperature and scale thickness at the time of measurement.

Another factor, that of temperature control, must be mentioned here, because the effective temperature may also be dependent on the rate of scaling. The scaling of iron is a combustion process in which a large amount of heat is evolved. If the scaling is rapid, as at the beginning of the process, especially in pure oxygen, this heat evolution may raise the temperature of the iron very appreciably above that of the surrounding atmosphere. This effect would of course cause iron and many other metals to burn up in air or oxygen at much lower temperatures if it were not for the protective action of the growing scale layer. This heating effect, though well known, has not always been taken into account in considering scaling rates; we shall mention it again later in connection with the experimental methods used in this investigation.

[12]D. W. Murphy, W. P. Wood and W. E. Jominy, "Scaling of Steel at Elevated Temperatures by Reaction with Gases and the Properties of the Resulting Oxides," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 193-232.

The remaining boundary condition necessary to permit of definite relations between scaling rate, time and temperature for a given metal, is the assumption that the degree of perfection of the contact between the different layers in the scale, and especially of the contact between inner scale surface and metal, does not change with time. The experiments of Pfeil combined with ordinary reasoning about the mechanism of scale formation leave no doubt that iron is taken up at the inner scale surface as well as oxygen at the outer surface, and that these diffuse in opposite directions through the scale. The inner iron concentration remains at a fixed maximum value only if perfect contact is maintained between scale and metal. The effect of "blistering" of the scale on the rate of scale growth is illustrated in some of the experiments described in this paper; it represents merely a break of intimate contact which interferes with the postulated constancy of the boundary conditions.

Mathematical Treatment of the Scaling Process at Constant Temperature

There can be no question that the process which determines the over-all rate of scaling is the rate at which the scaling agent can diffuse in to reach metal atoms and not the inherent rate of the chemical action involved; except possibly during the very first stage while the metal surface is still in part bare, in which case there may be interference by other factors of a type commonly designated as catalytic.

In order to apply the diffusion law to the rate of growth of scale, we choose first the simplest case of an infinite plane surface of a pure metallic element which forms only a single-phase layer of scale when exposed to the action of the corroding agent at constant temperature. This is in nearly all cases a gas or mixture of gases, but the discussion applies equally to the case of a liquid provided that it does not remove the scale by solution or erosion.

In the first place, we postulate that the effective concentration of the corroding agent at the exposed surface of the scale is constant. This condition is fulfilled exactly if the agent is a pure substance such as oxygen at constant temperature and pressure, less rigorously if the agent is diluted by an inert substance, as by nitrogen in atmospheric scaling. In this important case the effective concentration of oxygen at the surface of the scale is somewhat less than in the gas

as a whole; the magnitude of this deficiency is determined by the difference between the rate at which oxygen is taken into the scale and the rate at which diffusion and convection processes bring it through the gas layer in immediate contact with the scale. In general this deficiency is appreciable only in the initial stage of scaling, for only then does the rate of consumption of oxygen tend to be greater than the rate of supply. This postulate is therefore valid, except at the very beginning of scaling when indeed other factors play a role and no general treatment is possible; this limitation is therefore of no consequence in the present discussion.

In the second place, we postulate that the concentration of metal at the interface between scale and metal is constant, which implies perfect contact between scale and metal, and that the scale is continuous and free from cavities or cracks.

In the third place, we postulate that it is a two-way diffusion process, the corroding agent diffusing toward the metal, and the metal diffusing perpendicularly away from the interface, and that, since the two weight-concentrations are complementary, we may make use of the weight-concentration of one of them to describe the process in terms of a diffusivity constant D which we assume to be independent of the concentration and hence constant through the scale layer. On this basis we write the differential equation

$$D\frac{d^2u}{dx^2} = \frac{du}{dt} \qquad (1)$$

where u is the weight concentration of the corroding agent, at the time t in a plane at a distance x from the outer surface of the scale.

A solution of this partial differential equation which satisfies our particular conditions, is the well-known probability integral

$$u = A + B\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2} d\lambda \qquad (2)$$

in which the constants A and B are to be evaluated from the boundary conditions and λ is an integration variable. Differentiating equation 2 with respect to x, we get

$$\frac{du}{dx} = \frac{B}{\sqrt{\pi Dt}} e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2}$$

and therefore for the particular value X, which represents the position of the interface between scale and metal and thus corresponds to the thickness of the scale at any time, we have:

$$\left(-D\frac{du}{dx}\right)_{x=X} = -B\sqrt{\frac{D}{\pi}}\,\frac{e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2}}{\sqrt{t}} \qquad (3)$$

Now the left hand member of equation 3 represents the rate at which the scaling agent passes through the interface, and is therefore proportional to the rate of growth of the scale; or

$$\left(-D\frac{du}{dx}\right)_{x=X} = m\frac{dX}{dt} \qquad (4)$$

where m is a constant characteristic of the particular metal and corroding agent and is a measure of the thickness of scale produced per unit of corroding agent per unit area. Combining (3) and (4) we get

$$m\frac{dX}{dt} = -B\sqrt{\frac{D}{\pi}}\,\frac{e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2}}{\sqrt{t}} \qquad (5)$$

an ordinary differential equation which is identically satisfied if

$$x = \alpha\sqrt{t} \qquad (6)$$

where α is a constant which can be evaluated by the following steps. Substitution of this value of x into (5) enables us to evaluate the constant B; from our first and second postulates that the concentration at the surface u_o and that at the interface u_1, are constant, we find by appropriate substitution in (2) that $A = u_o$ and $u = u_1$; finally, reckoning time from the beginning of scaling, that is $t = 0$ when $x = 0$, we obtain

$$u_1 = u_0 - \frac{m\sqrt{\pi\alpha}}{2\sqrt{D}}\, e^{\left(\frac{\alpha}{2\sqrt{D}}\right)^2} \int_0^{\frac{\alpha}{2\sqrt{D}}} e^{-\lambda^2}\, d\lambda \qquad (7)$$

This equation defines α, which however, can only be evaluated graphically; and the value of α in turn determines, in accordance with equation (6), the rate of growth of the scale, in terms of the boundary conditions and the diffusivity coefficient. If all of the constants

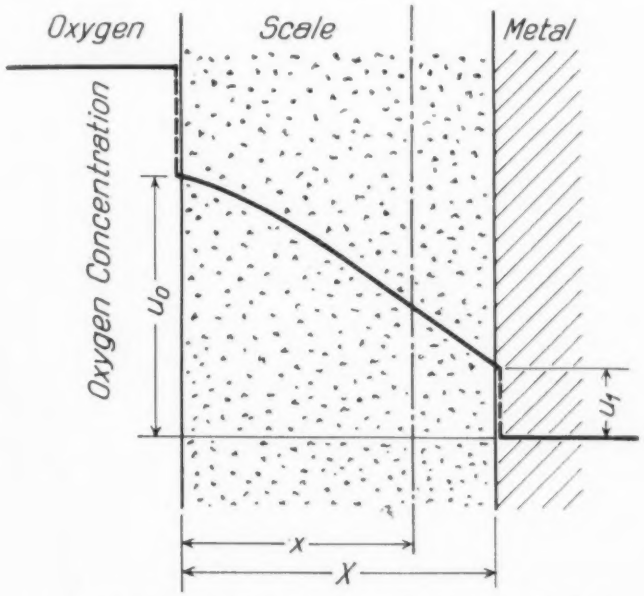


Fig. 2—Schematic Diagram Representing the Way in Which the Concentration u Changes Through the Scale Layer.

so evaluated are substituted in equation (2), it would represent the way in which the concentration u changes through the scale layer, as represented schematically in Fig. 2; the precise form of this curve is however of subsidiary interest at the present time.

The important conclusion is that embodied in equation (6): namely, that under the conditions specified, the thickness of scale is proportional to the square root of the elapsed time from the beginning of the process. This conclusion holds rigorously for an infinite plane surface in the ideal case, but is substantially true for many kinds of experimental specimens in which the edge effects are inappreciable. Similarly it holds for a cylinder provided that its

radius is large relative to the thickness of the scale, a condition which is not fulfilled with thin wires such as have frequently been experimented with. If we now make the plausible assumption that the increase of weight of the specimen on scaling is proportional to the thickness of the scale, this increase in observed weight should, in the ideal case, be proportional to the square root of the elapsed time. This conclusion does not hold for alloys generally, because there would in many cases be selective attack which would progressively alter the concentration of one or other of the constituents, particularly at the interface; nevertheless, when there is little difference in selective attack or only a small proportion of alloying element, the conclusion may be substantially valid for any given composition.

In steels, in which we are primarily interested, there is another complication, namely, that, as is evident from Fig. 1, the scale is composed of three distinct layers. Let us, therefore, consider the case of a multi-layer scale. The mathematical procedure for each layer is identical with that already given, there being one equation for each layer with constants characteristic of the layer. The sole difference is that one layer grows at the expense of another and equation (4) is replaced by an equation of the form

$$\left(-D_1 \frac{d u_1}{d x_1} \right)_{x_1 = X_1} - \left(-D_2 \frac{d u_2}{d x_2} \right)_{x_2 = X_2} = m \frac{d X}{d t}$$

As before, the equations are satisfied when $X_1 = a_1\sqrt{t}$, $X_2 = a_2\sqrt{t}$, etc., whence the total increase $x = X_1 + X_2 + \ldots = (a_1 + a_2 + \ldots)\sqrt{t}$; or, in this case also, the total thickness is proportional to the square root of the elapsed time. It may be noted, moreover, that the relative thickness of the several layers should remain constant.

Effect of Temperature Upon Rate of Scaling

The effect of temperature upon the rate of scaling depends primarily upon the variation of two factors: (1) the difference in total concentration or in solid solubility, within the scale layer; (2) the specific effective diffusivity coefficient D of the corroding agent through the scale. The former is a potential, analogous to voltage, the latter analogous to conductivity, in an electrical circuit. With change of temperature, there may also be a change in type of the

scale if it should pass through a transition region for the scale; but this case need not be considered further here.

In accordance with the ideal conditions postulated above, the concentrations at the boundaries of a scale layer are determined by, and equal to, the saturation concentrations of the solid solutions present; for example, in the scaling of iron in air, the outer surface of the FeO layer is saturated, at each temperature, with Fe_3O_4 (or excess oxygen atoms). The change in saturation concentration of a solid solution with temperature follows the usual equation for change of solubility with temperature, namely

$$\frac{d \ln N'}{dT} = \frac{Q}{R T^2}$$

where N is a measure of the concentration at the absolute temperature T, Q is the appropriate heat of solution and R is the gas-constant expressed in the proper units. On integration this has the form $u = K' e^{-\frac{Q}{RT}}$ on the assumption that no appreciable errors are introduced by substituting u, the weight concentration, for N, the mol fraction.

The variation of D with temperature follows, according to Dushman and Langmuir,[13] an equation of similar form, namely $D = k'' \delta^2 e^{-\frac{Q'}{RT}}$ where k'' is a constant characteristic of the reaction, δ the distance between atomic layers in the solid and Q' a heat term.

This identity of form of the equations representing the variation with temperature of the two factors concerned prevents us from separating the two effects; on the other hand it enables us to conclude that the influence of temperature upon the amount of scale W formed in a given time will be represented with reasonable accuracy by an equation of the form

$$W = K e^{-\frac{b}{T}} \qquad (8)$$

$$\text{or} \qquad \ln W = \ln K - \frac{b}{T}.$$

[13] S. Dushman and I. Langmuir, "The Diffusion Coefficient in Solids and its Temperature Coefficient," *Physical Review*, Vol. 20, Part II, 1922, p. 113.

where the constants K and b are evaluated from observations at two temperatures. It may be noted that, on this basis, a plot of log W against $\frac{1}{T}$, the reciprocal of the absolute temperature, should be a straight line. This conclusion is the same as that reached by Dunn[5] who, however, took into account only the variation of diffusivity coefficient, but not of solubility, with temperature; we agree with him in believing this exponential form of equation preferable to the purely empirical form $W = K T^n$.

Influence of Both Temperature and Time Upon Scaling

Combining equation 6, for time (t) alone, with equation 8 for temperature (T) alone, we obtain finally the form

$$W = a\sqrt{t}\ e^{-b/T} \qquad (9)$$

where W is the weight of corroding agent comprised in the scale—in other words, the increase in weight of the specimen—per unit of surface, and a and b are constants to be evaluated from the actual measurements. It will be shown that the observations on iron at various times and temperatures are in accordance with equation (9) in those cases in which the postulates underlying the derivation of the formula can reasonably be expected to be substantially fulfilled.

Experimental Method—The method used was to weigh, at appropriate intervals, the specimen suspended in a vertical tube furnace maintained at constant temperature. The specimen was in the form either of a rectangular plate or of a round-ended cylinder; its surface ranged from 30 to 90 square centimeters.

A small Globar-type tube furnace, with its axis vertical, was set up with a potentiometer controller so that its temperature could be regulated within a few degrees anywhere in the range 500 to 1200 degrees Cent. (930 to 2190 degrees Fahr.); above it an ordinary balance was placed, properly shielded from heated currents from the furnace, so that a platinum wire, attached to one arm of the balance, extended down through a small hole in an insulating plug, and supported the specimen inside the furnace. Contact between suspending wire and specimen was obviated by a short piece of two-hole procelain protective tube set into a hole through the specimen. Temperature was measured by a platinum, platinum-rhodium couple

located close to the specimen; at the higher temperatures where the rate of heat evolution accompanying the scaling sufficed to raise the temperature of the specimen appreciably above that of the furnace, a second thermocouple was passed through the second hole of the porcelain protective tube so that its junction was within the specimen. The lead-in wires of this couple extended through fine porcelain tubes, attached to the suspending wire, to a point outside of the furnace, and arranged there so that the extension leads to the ice junction could be hooked on for temperature measurements and unhooked during weighing; the use of this second thermocouple gave noticeably more reproducible results. The change in weight of the specimen produced by scaling was observed at suitable intervals, with an accuracy of $\pm$ 2 milligrams.

In the few experiments made in an atmosphere of steam or carbon dioxide a porcelain tube, with lower end closed, was placed in the tube furnace, and a current of steam from a boiler, superheated by a small tubular furnace to around 500 degrees Cent. (930 degrees Fahr.) was delivered to a level below the specimen through a thin silica tube and allowed to pass up around the specimen at a linear velocity of about 50 feet per minute, escaping upwards through the hole for the suspension wire and attached thermocouple.

Tests were run for long periods, ranging from 20 to 150 hours, to ensure that the scale thickness was great enough, during the larger part of the run, so that the scaling rate would not be limited by slow diffusion in the gas phase. This has the additional advantage that the control of the rate of gas flow becomes practically unimportant. In the tests in air, only the natural rate of circulation brought about by the chimney effect through the rather open Globar furnace was used; in the other experiments, only a single rate of flow was used.

Scaling Data for Commercially Pure Iron

The results for specimens of commercially pure iron in air at a series of constant temperatures between 550 and 1100 degrees Cent. (1025 and 2010 degrees Fahr.) are presented in Fig. 3, plotted on logarithmic scales for both time (in minutes) and weight of oxygen absorbed (in milligrams per square centimeter). The log-log plot was used because it has three distinct advantages: (1) it enables one to picture the whole course of the experiments, which extended up to nearly 10,000 minutes, with constant percentage accuracy; (2)

it presents any simple power function, such as the square root relationship postulated, as a straight line, the slope of which corresponds to the exponent, one-half in this case; (3) it shows immediately if this exponent is constant for variation of a factor such as temperature, by the parallelism of the several lines. The lines in Fig. 3 were all drawn with a slope of ½, the ideal slope indicated by the mathematical discussion; and it is obvious that the data tend

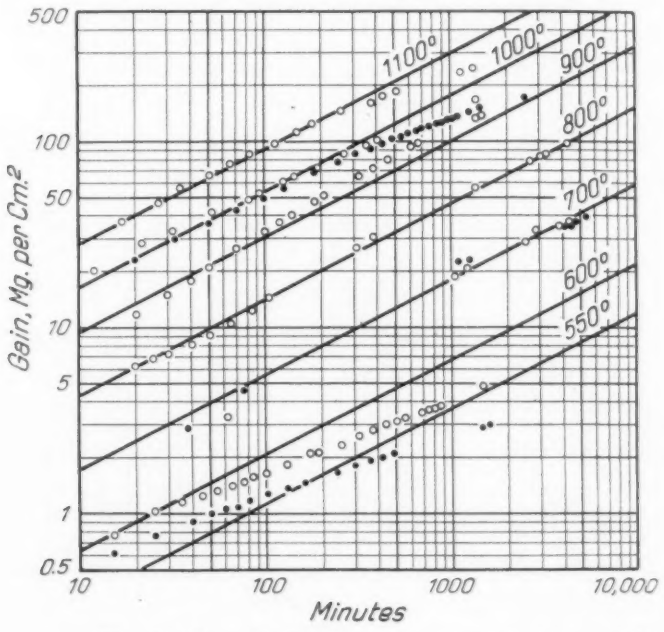


Fig. 3—Time Scaling Data for Iron in Air at 1100 Degrees Cent.

definitely to follow these lines. (It should be remembered that on this scale the right hand portion of the curves correspond to relatively long time intervals.) It was not considered necessary to tabulate any of the experimental results because the curves reproduce them with as much real accuracy as is inherent in such data.

There are, however, very noticeable deviations from the square root relationship, especially at 600 and 550 and also at 1000 degrees Cent. (1110, 1025 and 1830 degrees Fahr.). The question immediately arises as to whether this deviation indicates that the square root relationship does not hold exactly even under the ideal conditions assumed in its derivation above, or whether one of these ideal conditions is not fulfilled in such cases. It was noticed, as the tests proceeded, that the specimens with the smoothest and most uniform scale also gave the closest approximation to the square-root relation-

ship with time, whereas those showing deviations always had very noticeable blisters or swellings in the scale. A scaling test on pure copper at 900 degrees Cent. (1650 degrees Fahr.) was made, in which the scale formed was very smooth and uniformly adherent, and the variation of scaling with the square root of time was very closely approximated. Later, after two runs on iron at 700 degrees Cent. (1290 degrees Fahr.) which apparently followed the ideal curve fairly closely, a third run on iron at 700 degrees Cent. in which very many readings happened to be taken, gave a very different curve, and the specimen had finally large blisters over nearly its whole surface. These extremes are illustrated by the curves in Fig. 4, the attached pictures showing the appearance of the corresponding specimens after scaling. In the case of the iron specimen at 700 degrees Cent. very large blisters must have swelled out gradually, beginning early in the test, and the rate of scaling gradually decreased below the ideal rate; after about 250 minutes these blisters must have cracked away from the specimen, exposing again to the air a large surface of metal with only a very thin scale coating, and the rate then changed to a high value which slowed down again as new blisters were formed.

Obviously if blisters are formed in part of the area, the continuity of the scale is not constant and the second condition postulated above in the ideal case is not fulfilled. For such cases the corresponding square root curve in Fig. 3 usually represents a maximum rate, the actual rate of scaling dropping more and more below this curve as blistering occurs; this effect is taking place in the latter part of the 1100 degrees Cent. (2010 degrees Fahr.) curve, one of the curves at 1000 degrees Cent. (1830 degrees Fahr.), also in the 600 degrees Cent. (1110 degrees Fahr.) curve. In many of the curves which fall below the limiting square root curve owing to blistering of the specimen, there is a tendency for the slope to fall away and increase later up to the square root slope again. This is noticeable in the 600 degrees Cent. curve in Fig. 3, where several parts of a curve drawn through the points would be parallel to the square root line. Although we have no positive evidence, we believe it probable that small blisters swell up, slowing the rate of oxygen diffusion at these areas, but as scaling progresses, the growth of scale under these blisters would tend, by closing up any such spaces, to re-establish the continuity of scale growth pre-requisite to the ideal rate.

By plotting the intercepts of the curves for one material at vari-

ous temperatures (Fig. 3) on any vertical line, which represents a constant time interval, we obtain directly the variation of scaling rate with temperature. Such intercepts, for commercially pure iron from Fig. 3 and for pure copper from the paper by Pilling and Bedworth,[1] are plotted in Fig. 5 in terms of log W, the logarithm of the weight increase, against 1/T, the reciprocal of the absolute temperature. The fact that these graphs are straight lines is in accordance with our conclusion on a previous page, as expressed in equation 8. This implies therefore that if we have measured the growth of a given scale at two temperatures, we may by means of equation 8 calculate the growth of the same scale at any other temperature.

It would not necessarily hold if extrapolated into a temperature range in which other solid phases appear in the scale. For instance, the lowest curve in Fig. 3 is that extrapolated to 550 degrees Cent. (1005 degrees Fahr.) from Fig. 5, whereas the observations at this temperature do not fall on this line even in the early period before blistering began; but since the FeO phase is not stable below 575 degrees Cent. (1070 degrees Fahr.) (see Fig. 1), the character of the scale may well be quite different with respect to diffusion below this temperature. On the other hand, the transition in the iron itself, from γ to α, appears to exert no appreciable influence upon the rate of scaling.

We now have the data requisite for the evaluation of the two empirical constants of equation 9, and obtain:

for commercially pure iron $$W = 6.30 \sqrt{t}\, e^{-\frac{9000}{T}}$$

for pure copper $$W = 12.8 \sqrt{t}\, e^{-\frac{10600}{T}}$$

where W represents the gain in weight in grams per square centimeter surface of the specimen, t is time in minutes, and T absolute temperature in degrees centigrade. For purposes of calculation it is more convenient to have them in the logarithmic form, namely

for iron $$\log W = .7993 + \tfrac{1}{2} \log t - \frac{9000}{2.303\, T}$$

for copper $$\log W = 1.0821 + \tfrac{1}{2} \log t - \frac{10600}{2.303\, T}$$

It is of interest to note that our single measurement on copper at 900 degrees Cent. (1650 degrees Fahr.) (upper curve, Fig. 4) proves by this mode of calculation to be concordant with those of Pilling and Bedworth; and that the latter's data on ingot iron in air at 800, 900 and 1000 degrees Cent. (1470, 1650 and 1830 degrees Fahr.) (as tabulated on page 569 of their paper) agree with ours within a few per cent. Their values for ingot iron in oxygen are about twice as high as in air; this difference may however be ascribed to a higher effective temperature of the specimen in oxygen than in air, for the same furnace temperature, corresponding to the more rapid development of heat by the process of oxidation.

We conclude therefore that for commercially pure iron between 600 and 1100 and perhaps up to 1200-1300 degrees Cent., and for pure copper between 600 and 1000 degrees Cent., the respective formulas given above represent satisfactorily the amount of oxygen absorbed in scaling, provided always that the scale is thick enough so that the rate of supply of oxygen by diffusion in the gas phase is not a limiting factor, and that there is no blistering or other discontinuity in the scale layer.

Scaling Rates in Steam and in Carbon Dioxide

Increased rates of scale formation in steam have been reported by Murphy, Wood and Jominy,[14] by Upthegrove and Murphy,[15] by W. Schroeder[16] and by Marson and Cobb.[17] Although in our work the effect of variation in the gas phase was not of primary importance, two tests in steam, at 700 and 1100 degrees Cent. (1290 and 2010 degrees Fahr.) and two in CO_2, at 900 and 1100 degrees Cent. (1650 and 2010 degrees Fahr.) were made as a check upon the data in the papers cited. The samples were of the same material as was used for the runs shown in Fig. 3; the linear rate of gas flow past the specimen

[14]D. W. Murphy, W. P. Wood and W. E. Jominy, "Scaling of Steel at Elevated Temperatures by Reaction with Gases and the Properties of the Resulting Oxides," Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 193-232.

[15]C. Upthegrove and D. W. Murphy, "Scaling of Steel at Heat Treating Temperatures," Transactions, American Society for Steel Treating, Vol. 21, 1933, p. 73-96.

[16]W. Schroeder, "Untersuchungen über den Einfluss von Liegedauer Temperatur, Geschwindigkeit und Atmosphäre auf den Eisenabbrand." (Influence of time of exposure, temperature, gas velocity and nature of atmosphere on scaling), *Archiv Eisenhüttenwesen*, Vol. 6, 1932, p. 47-54.

[17]C. B. Marson, and J. W. Cobb, "Scaling by Air, Water Vapor, and Carbon Dioxide," *Journal*, Society Chemical Industry, Feb. 25, 1927, p. 61-71T.

was about 50 feet per minute for both steam and carbon dioxide. The results are shown in comparison with those in air at the same temperatures in Fig. 6. The points observed in steam at 700 degrees Cent. approximate to the ideal slope less accurately than the corresponding points in air; but the difference in total amount of oxygen absorbed is hardly greater than the irregularities caused by blistering in the scale formed in air. At 1100 degrees Cent. the rate of scale growth in steam is somewhat faster than the square root line, but approaches this slope near the end of the run; the total amount of oxygen absorbed in steam is quite appreciably greater than in air, particularly towards the end of the run, where the rate in air dropped off because of blistering.

During the first 100 minutes in CO_2 at 900 degrees Cent. the amount of scaling was only about 40 per cent of the "ideal" rate in air at this temperature (see Fig. 6). The relative difference decreased gradually with time up to about 600 minutes, after which period the scaling in CO_2 was about 75 per cent of that in air at the same temperature. From 600 to 4300 minutes, in CO_2 at 900 degrees Cent., the scaling rate followed the square root relationship very closely. At 1100 degrees Cent. in CO_2 the square root law was obeyed for nearly the whole period of scaling with only about 10 per cent less scale formed than in air at the same temperature.

After 4300 minutes, in the run with CO_2 at 900 degrees Cent., the atmosphere was changed to pure oxygen (see point A in Fig. 6) and the scaling continued with no other change in conditions for about 4000 minutes additional time. The scale weight increased rapidly at first in the oxygen (probably due to the rapid oxidation of the outside portion of the "ferrous" layer present in CO_2, to form layers of Fe_3O_4 and Fe_2O_3), but, as the points approached our "ideal" air curve for 900 degrees Cent., the rate of increase dropped off to give a close approximation to the ideal curve. This result tends to confirm the statement made earlier in this paper, to the effect that scaling rates in pure oxygen should be the same as in air, when the so-called ideal conditions are maintained.

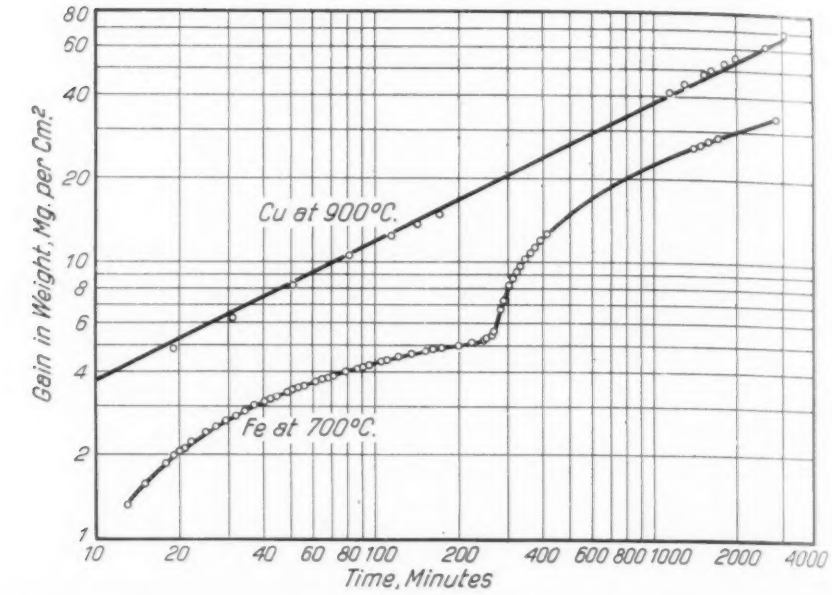
It should be emphasized that the CO_2 and H_2O used in these experiments were not absolutely pure. The steam contained small traces of air, and the CO_2 (taken directly from an ordinary tank) was not absolutely free of moisture and free oxygen. Very dry, oxygen-free carbon dioxide might give different results, especially in short time experiments, due to the absence of possible catalytic effects

of small concentrations of H_2O or O_2 molecules. Such pure gases never occur in practice, however, and in any case these effects are not important here, since we are considering only the problem of diffusion rates in the scale layer, independently of any questions of varying rates of supply of the scaling agent from the gas phase.

Although our results differ widely from certain data in papers cited above (Refs. 14-17), the discrepancy is to some extent more apparent than real. We agree qualitatively to the extent of finding increased scaling in steam and decreased scaling in carbon dioxide, but it seems obvious that these differences become less and less with longer periods of exposure, and that the process is much more regular and predictable over longer periods than for short ones, in which many other factors such as gas diffusion rates, adsorbed gas films, blistering, etc., may obscure and overshadow the effects as limited simply by diffusion in the scale layer. Marson and Cobb's very low values in CO_2, for example, may be due to the absence of the catalytic effects of traces of water vapor, probably absent in their very highly purified gas. Upthegrove and Murphy's decreased rates with rising temperature in air between 1800 and 2000 degrees Fahr. shown in Fig. 3 of their paper are unexpected but may be caused by blistering in the scaled pieces in this range, a condition which is in general neither typical nor reproducible.

Apparently, therefore, the square root relationship developed on the basis of a diffusion process holds fairly well for long exposure in CO_2 and H_2O atmospheres. The rate of scaling in both of these gases at a given temperature might be expected to be somewhat less than in air since the total range of oxygen "pressure," or concentration, between the outer and inner surface of the single scale layer produced in steam or CO_2 is less than for the three-layer scale formed in air. The data on CO_2 are in accord with this expectation, but in steam at 1100 degrees Cent. (2010 degrees Fahr.) the rate is towards the end 60 per cent greater than in CO_2; the only observable difference is that the scale from steam is relatively porous, as is illustrated in Fig. 7, whereas the scale from CO_2 shows very slight porosity yet the same microstructure.

The scaled pieces, after the runs both in steam and carbon dioxide, looked quite different from those heated in air. The surface of the scale on samples heated in air, when not blistered, was quite smooth, with a velvety, finely crystalline sheen, whereas that of the scale formed in CO_2 or steam was rough and coarsely crystal-



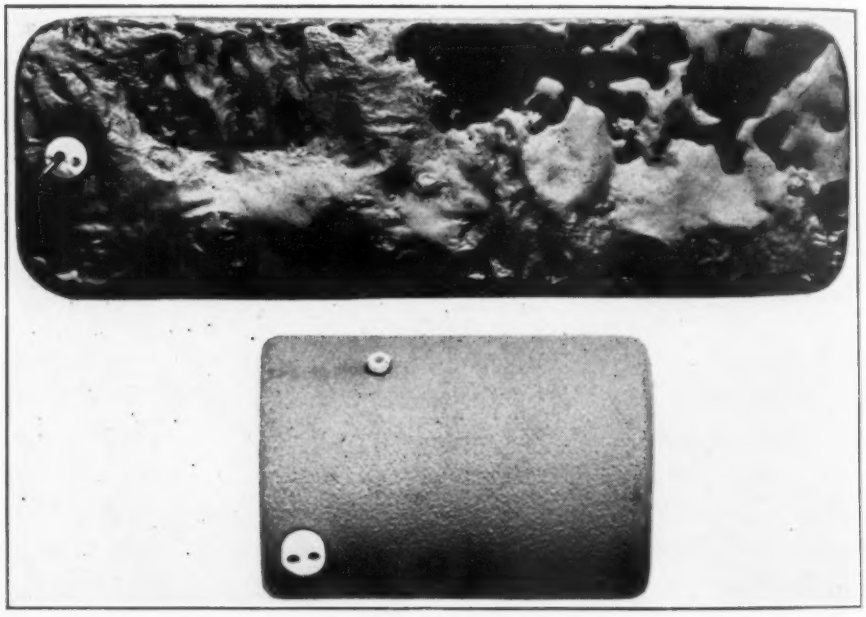


Fig. 4—Comparison of a Smooth and Blistered Scale.
The Upper Photograph Represents Iron at 700 Degrees Cent.
The Lower Photograph Represents Copper at 900 Degrees Cent.

line with many crystal facets at varying angles to the surface. Under the microscope, the cross sections were found to consist only of a single layer, like the inner ferrous layer depicted in Fig. 1; X-ray analysis also showed the simple cubic lattice of FeO to be the predominant crystal form. The scale formed at 1100 degrees Cent.

(2010 degrees Fahr.) in steam is shown in the photomicrographs (Fig. 7) which include the complete layer, showing the junction with the iron surface, at 50 diameters, and a field at 500 diameters showing the bright Fe_3O_4 crystals which separated from the FeO solid solution during cooling. The scale produced both in steam and CO_2 also showed almost no tendency to crack or to separate from the iron during cooling, and did not blister; this is probably correlated with the fact that in these atmospheres the scale forms in a

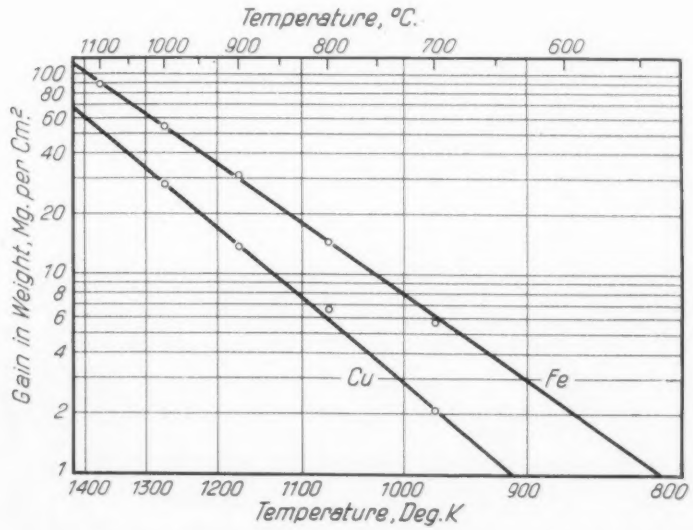


Fig. 5—Gain in Weight of Iron and Copper in Air at Various Temperatures for 100 Minutes. Plotted on a Scale of log W versus $\frac{1}{T}$

single layer, whereas in air the simultaneous formation of the FeO and Fe_3O_4 layers, whose density and thermal expansion differ, causes the cracking and blistering usually encountered.

It is rather surprising that no layer of Fe_3O_4 formed in these tests in view of the fact that at equilibrium, Fe_3O_4 should be the stable oxide in steam or CO_2 even with appreciable amounts of hydrogen or CO present. Fe_3O_4 might, however, not be formed on the outer surface faster than it could dissolve into the FeO layer. Moreover the presence, in the film of relatively quiet gas in immediate contact with the surface, of hydrogen or CO, which are the products of reaction, might slow down the rate of Fe_3O_4 formation to the point at which no magnetite layer would be formed. If these tests had been run long enough, an Fe_3O_4 layer would probably have formed as the scale grew thicker and absorbed oxygen more slowly

from the gas phase. It is probable that the use of steam in the Bower-Barff oxide coating process for iron, which gives an adherent scale is effective partly because the total scale thickness is small, but also largely because it consists almost entirely of a single layer of ferrous oxide.[18]

Scaling Rates for a Few Binary and Ternary Alloys of Iron

The growth of scale on a number of common alloys of iron, all heated at 1100 degrees Cent. in air, is illustrated in Fig. 8 and compared with that for pure iron (upper curve). Because of the double log scale used, as in Figs. 3, 4 and 6, this figure represents a very large range in scaling rates.

No binary alloy can be expected to scale exactly according to the square root of elapsed time at constant temperature, since one boundary condition postulated, namely, that the composition of the metal layer adjacent to the inside of the scale remain constant with time, is likely not to hold because of differences in rate of oxidation of the components and in the oxygen pressures of their oxides. For example, in a carbon steel, the metal layer under the scale is slowly decarburized as scaling progresses. As shown by Fig. 8, however, the disturbing effect of this factor may be less than the disturbance due to blistering, etc., which may be present even with pure metals, for the points for 0.9 per cent carbon steel, 4 per cent aluminum steel, and 35 per cent Ni-Fe alloy, all follow nearly the ideal slope. Pilling and Bedworth have shown that this square root curve is followed closely by Cu-Ni alloys between 0 and 35 per cent and between 80 and 100 per cent nickel but not by alloys of intermediate composition.

The 0.9 per cent carbon steel absorbs oxygen only slightly more slowly than pure iron; if we allow for the oxygen which must have formed CO or CO_2 with the carbon and diffused away, this difference becomes very small, so that for practical purposes, the effect of carbon on scaling rate may be regarded as negligible.

The presence of 4 per cent aluminum cuts the scaling rate to about one-half, 35 per cent nickel only to about one-third, that of pure iron. In the 18 per cent chromium—8 per cent nickel alloy, the rate of scaling in the earlier periods is around one-fifth of that

[18] R. M. Bozorth, "Structure of a Protective Coating of Iron Oxides," *Journal*, American Chemical Society, Vol. 49, 1927, p. 969-76.

for pure iron, but this difference decreases with time, the growth of scale on this alloy being not even approximately proportional to the square root of time. For the alloys with 8 and 16 per cent aluminum and with 27 per cent chromium, we have types of curves quite different from those for the pure metals, with the rate of scaling decreased in the last two alloys to roughly 1/100th of the value for pure iron at the same temperature.

The three aluminum alloys tested happen to show a transition from one type of scale formation to an entirely different type with the higher aluminum contents. The scale formed (Fig. 9) on the

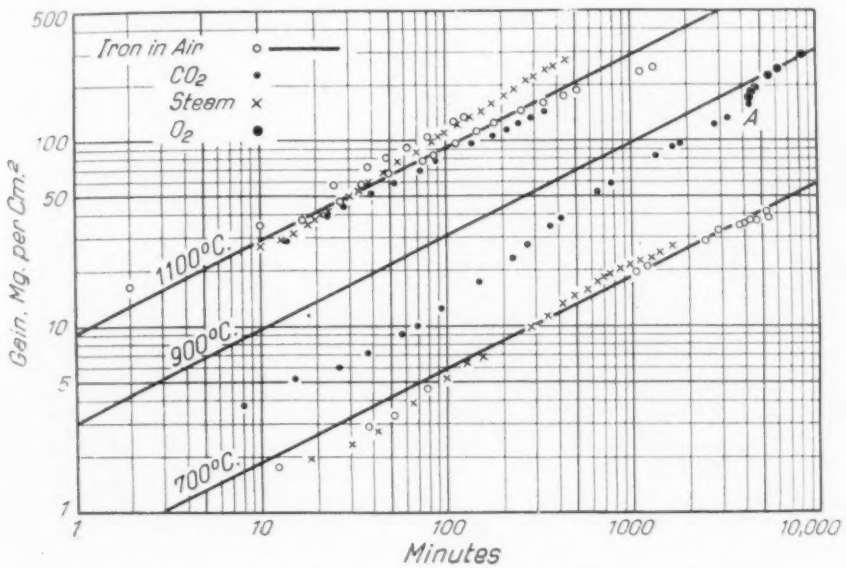


Fig. 6—Time-scaling Data for Iron in Various Atmospheres.

4 per cent aluminum-iron alloy is the same in appearance as on pure iron. The aluminum atoms in the metal must oxidize to Al_2O_3 as fast as they are exposed by the penetration of scale. Very little good information is available on the system comprising Al_2O_3 and iron oxides; the Al_2O_3 may be in solid solution in the FeO layer, or may form tiny Al_2O_3 grains or possibly be present as Al_2O_3-FeO spinel molecules distributed in the scale. Whatever its form, there is apparently not enough Al_2O_3 present to form a continuous phase at any point, and the net effect is merely a moderate reduction in scaling rate due to a lessening of the effective area for diffusion or of diffusivity. In the initial stage of the scaling process on the 8 per cent aluminum alloy, on the other hand, any iron oxide which may have formed initially at the metal surface was presumably re-

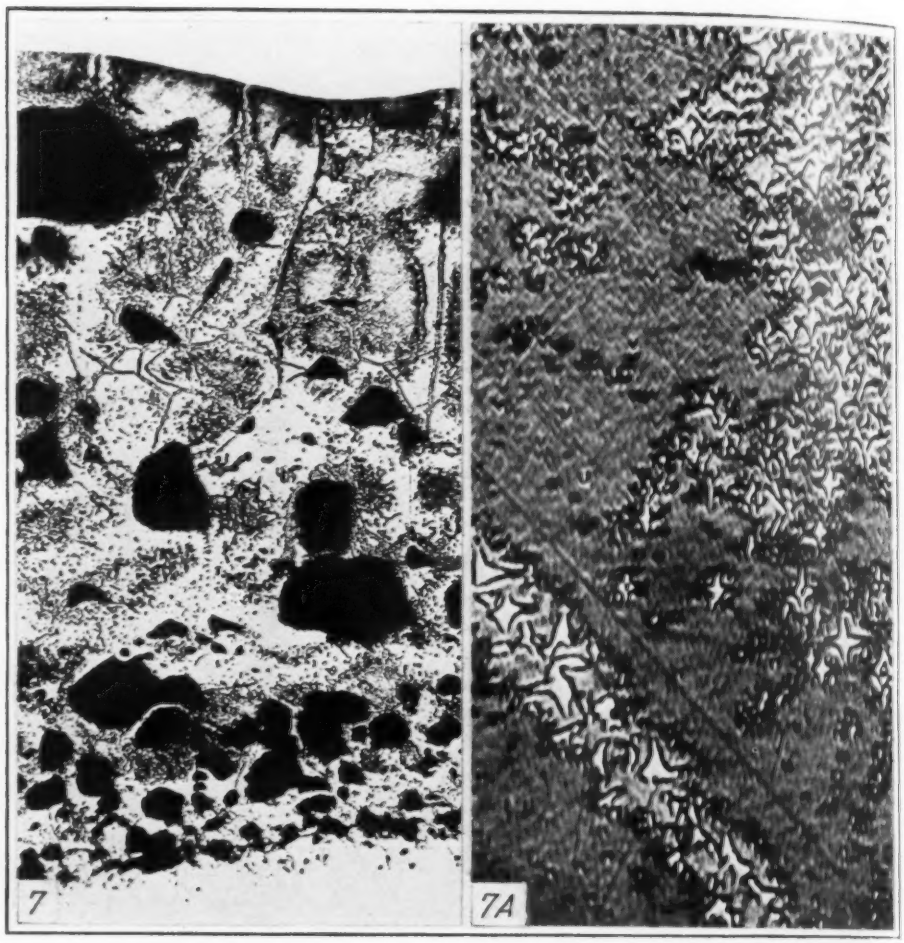


Fig. 7—Cross Section of Scale Formed on Iron at 110 Degrees Cent. in Steam. Fig. 7 at × 50; Fig. 7A at × 500.

duced to metal by aluminum diffusing out, so that a white, coherent, protective film, composed essentially of Al_2O_3, was formed over the surface, through which oxygen diffused so slowly that more aluminum atoms were supplied by diffusion fast enough to unite with all the oxygen available and so prevent the formation of any appreciable amount of iron oxide. During this initial stage the scaling was very slow, as shown by Fig. 8. After a time, however, the rate of scaling begins to rise, and this undoubtedly coincides with the appearance of the black iron oxide nodules shown in the middle sample in Fig. 9. Apparently, at a few spots in the surface, the supply of aluminum atoms could not keep pace with the supply of oxygen atoms coming through the film, resulting in the formation

of some iron oxide, which pushed out or dissolved the Al_2O_3 and caused a break in the continuity of the Al_2O_3 layer; oxygen then was able to diffuse in faster, more iron oxide was formed and the black iron oxide spot spread rapidly. Polished sections of these nodular scale areas look almost exactly like the scale on pure iron, with the same three oxide layers present as are shown in Fig. 1.

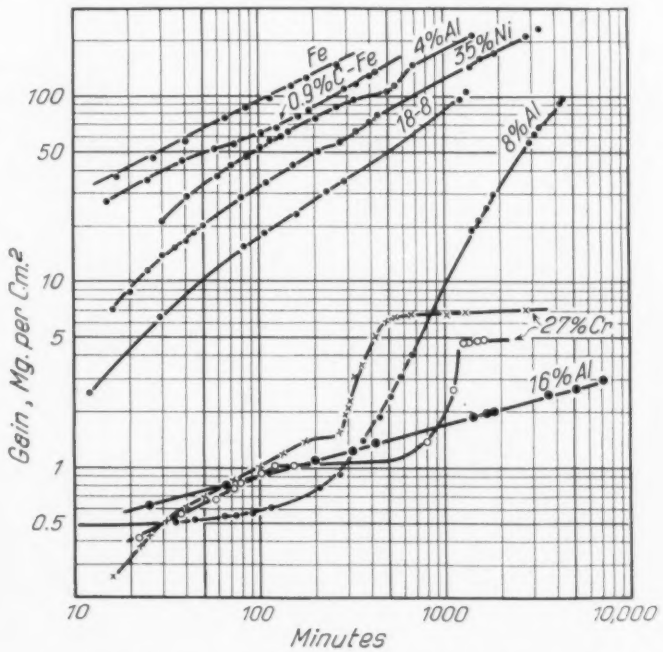


Fig. 8—Time-scaling Data for a Few Alloys of Iron in Air at 1100 Degrees Cent.

On the 16 per cent aluminum alloy, the white protective aluminum oxide scale coating persisted unbroken to the end of the test, which in this case was extended to about 117 hours; apparently in this alloy there is enough excess aluminum so that the supply of aluminum by diffusion to the surface could more than keep pace with the supply of oxygen diffusing through the scale. Curiously enough, the points for this alloy fall almost exactly on a straight line on the log-log plot, but its slope is low, indicating that the rate of scaling decreases at a much more rapid rate than demanded by the square root relationship. It should be noted that in these iron-aluminum alloys with 4, 8 and 16 per cent aluminum by weight, the corresponding atomic percentages of aluminum are 8, 15.2 and 28.4 per cent respectively, so that in the 16 per cent aluminum alloy there is nearly one atom of aluminum for every three atoms of iron.

As noted above, von Schwarze[4] describes exactly the same phenomena in a series of aluminum alloys, giving the "transition range" in which both the black and the white type of scale were formed as between 7 per cent and 10 per cent aluminum. A paper by Ziegler[19]

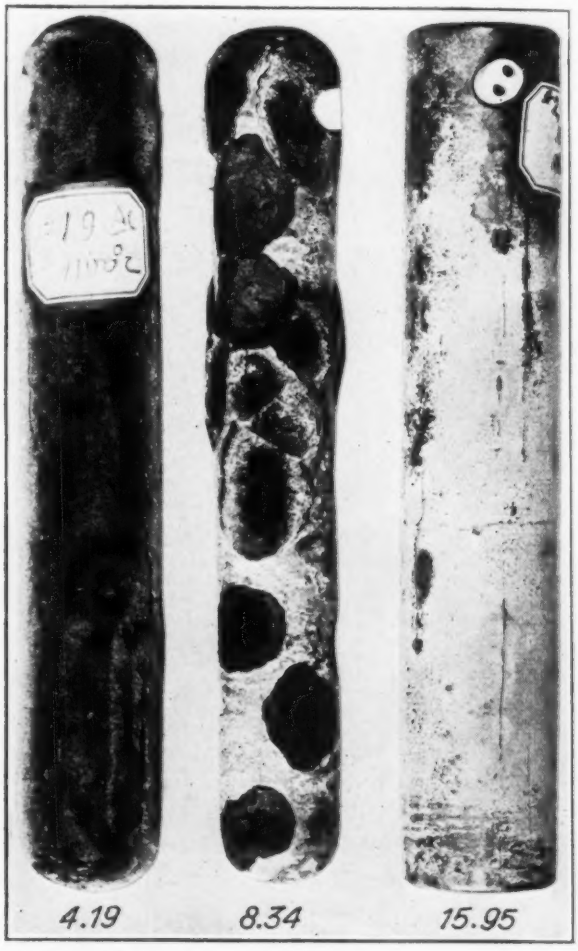


Fig. 9—Iron-Aluminum Alloys at 1100 Degrees Cent. The figures under each specimen represents the aluminum content.

on the oxidation of iron-aluminum alloys, however, shows a smooth and gradual change in scaling rates between 0 and 8 per cent aluminum. These data, which apparently were all obtained from 2-hour periods of exposure, constitute another example of the tendency to shorten up the period so much that the scaling behavior observed is not completely typical of the metal over longer periods.

[19]N. A. Ziegler, "Resistance of Iron-Aluminum Alloys to Oxidation at High Temperatures," American Institute of Mining and Metallurgical Engineers, Technical Publication No. 450, February, 1932.

The 27 per cent chromium-iron alloy gave the same peculiar type of curve in three check runs, using differently shaped and treated pieces. At first the scaling proceeds slowly and uniformly at about the rate for the 16 per cent aluminum alloy, following approximately the square root relationship with time, but after a certain period, the scale apparently breaks up slightly and allows fresh metal surface to be exposed; scaling is then very rapid for a short time, but soon the scale structure becomes closed up and coherent again, after which the rate becomes extremely slow and remains so, at least up to 50 hours at 1100 degrees Cent. (2010 degrees Fahr.). We have not studied the scaling of a series of iron-chromium alloys in detail, and have no explanation of this rather peculiar behavior.

The information gained from these tests and from the observations recorded in the literature furnishes little indication of what would be a logical procedure in a search for a ferrous alloy highly resistant to scaling at elevated temperatures. The obvious requirements are that the alloy should form a closely adherent surface film of oxide, and that this film should be nearly impervious to the passage of oxygen atoms inwards or of metal atoms outwards; but as to the implications of these requirements, one can only raise questions which can be answered only by specific investigation. For instance, does close adherence of scale imply that the pattern of the metal atoms in the scale film is nearly identical with the arrangement of those metal atoms in the surface skin of the specimen? or even that there is one network of metal atoms common to both scale and metal surfaces at the interface? or merely that the effective expansion coefficients of scale and metal in the plane of the interface must be nearly alike? Should the alloying element have a high rate of diffusion through the iron matrix, so that it comes rapidly to the surface to heal up imperfections in the scale? and must it be more readily oxidizable than iron, as aluminum and chromium are? Is a highly impervious oxide layer one in which oxygen or metal is almost insoluble? Is it an oxide of a metal which forms a single stable oxide, as Al_2O_3, rather than of such as iron with its several oxides and oxide mixtures, and is it likely to be a compound oxide, such as a spinel? On questions such as these present knowledge is largely or entirely lacking; until some of them are answered one is limited to purely empirical tests most of which are certain to be unsuccessful.

Conclusions

On the basis that the scale on a metal which forms a compact scale grows by a process of simple diffusion through the scale layer already formed, scaling at constant temperature should, in the ideal case, be proportional to the square root of the time. We have found that the scaling of iron satisfactorily follows this proportionality for longer periods of exposure; and that for a given period of exposure the variation with temperature is exponential with respect to the reciprocal of the absolute temperature. The observed limiting rates for commercially pure iron and pure copper are in close accordance with the following formulas, strictly applicable only to specimens bounded by infinitely extended planes, but close approximations for all ordinary shapes, except thin wires.

for iron, at temperatures 600-1100° C. $W = 6.30 \sqrt{t}\ e^{-\frac{9000}{T}}$

for copper, at temperatures 600-1000° C. $W = 12.08 \sqrt{t}\ e^{-\frac{10660}{T}}$

where W = oxygen absorbed in grams per square centimeter of surface area, t is time in minutes, T is absolute temperature in degrees K, and e is the base of the natural logarithms.

In the scaling of iron, the "ideal" conditions are sometimes not fulfilled, owing to a marked tendency toward blistering and the formation of cracks in the complex, three-layer scale formed on iron in air. This tendency toward irregular growth is not nearly so marked in an atmosphere of steam or CO_2, in which a single layer scale usually forms, with a much better adherence of the scale to the metal.

Substitution of commercial carbon dioxide for air lessens somewhat the rate of scaling of iron, especially during the first few hours of exposure, in the temperature range 900-1100 degrees Cent. (1650-2010 degrees Fahr.); in steam at 700-1100 degrees Cent. (1290-2010 degrees Fahr.) the scaling rate is somewhat greater than in air. As the period of exposure increases the relative differences caused by variation of gas composition decrease, and the square root relationship is followed more closely both in H_2O and in CO_2. The greater rate of scaling in steam is probably connected with the fact that the scale formed in steam was considerably more porous. The

scale formed both in CO_2 and in H_2O is practically a single layer of the ferrous oxide solid solution; and this scale shows much less tendency toward blistering than that formed in air.

The above relationships do not necessarily hold for alloys of iron or copper. Nevertheless, from the few tests on iron alloys, we conclude that carbon, up to 1 per cent at least, has practically no effect upon scaling rate. Nickel up to 35 per cent or aluminum up to around 5 to 7 per cent reduces scaling only moderately, to perhaps around one-half to one-third of the amount for pure iron, with the square root of time relationship approximately followed. Aluminum above 12 to 14 per cent cuts the scaling rate down to a magnitude of 1/100 of that for pure iron, and a 27 per cent chromium-iron alloy is nearly as effectively protected against scale growth at temperatures up to above 1200 degrees Cent. (2190 degrees Fahr.) as these high-aluminum alloys. Von Schwarze found that a ternary Fe-Cr-Al alloy containing as little as about 2.5 per cent chromium and 10 per cent aluminum gave very good protection up to about 1200 degrees Cent. (2190 degrees Fahr.).

THE EFFECT OF HYDROGEN ON THE TRANSFORMATIONS IN IRON

By R. H. Harrington

Introduction

IN the August 1933 issue of Transactions appeared an article[1], concerning the subject of the above title, which was contributed by Dr. Hans Esser and Heinz Cornelius and based upon their own excellent researches. Had they confined themselves accurately to the subject of their research, the present writer could do nothing but commend the excellence of their scientific methods and the importance of their results in showing that hydrogen *is one* of the factors that may cause two-stage allotropy. However, in referring to previously published work by Professor W. P. Wood and the writer[2,3], Messrs. Esser and Cornelius have made many grave errors in misquotations from our papers and several very important omissions and misinterpretations in the reading thereof. We can only account for this by assuming that it was necessary to translate our papers into German and that the losses were incurred in this manner. Space will not be taken at this time to completely correct the errors but a few of the more important points must be cited.

Discussion

The following statements in quotation marks are direct quotations from the paper by Esser and Cornelius. The statements without quotation marks may be found, either word for word or in

[1]Hans Esser and Heinz Cornelius, "On the Influence of Hydrogen on the Transformations in Iron," Transactions, American Society for Steel Treating, Vol. 21, August 1933, p. 733.

[2]R. H. Harrington and W. P. Wood, "Iron-Carbon Critical Ranges," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 632-658.

[3]R. H. Harrington and W. P. Wood, "Allotropy in Iron and Steel," Transactions, American Society for Steel Treating, Vol. 20, December 1932, p. 529-548.

This paper is a discussion of the paper by Esser and Cornelius which appeared in the August 1933 issue of Transactions. The author, R. H. Harrington, is research metallurgist, General Electric Co., Schenectady, N. Y. Manuscript received September 7, 1933.

essential meaning, in the previous publications by Prof. Wood and the writer.

1. "The most important result of this work (that of Harrington and Wood) is the proof that the A_3 and A_1 transformations take place in two stages which can be recognized as separate effects on the *differential* thermal analysis curves." As a matter of fact, the inverse-rate method was used throughout our work, and, we believe, has advantages over the differential method in this particular application.

2. "Such double effects have *not* been observed by earlier writers." Several references to previous records are given in our bibliographies, papers, and the printed discussions following the papers. These give instances of double points. In none of these instances could the doubling of allotropy be ascribed to hydrogen.

3. Esser and Cornelius have apparently overlooked the fact that our analyses were made in vacuum. They have conclusively shown that this eliminates hydrogen as a cause of doubling of allotropic points. On a like basis we had already come to believe that in our work the hydrogen had been eliminated as a factor, especially in repeated runs. As we had indicated, it is quite probable that some other composition factor was responsible for the doubling observed in our work. The theory of two-step allotropy is independent of the identity of this composition factor.

4. Esser and Cornelius point out that the diagram drawn from points on the heating curves from our data differs from the standard iron-carbon constitutional diagram. The two should not be compared. We do suggest that logical comparisons can be made between the standard diagram and that obtained from averaging the heating and cooling transformations as observed by us. Such an "averaged" diagram appears in Fig. 8 of our first paper[2].

5. "The two effects which were found (by Harrington and Wood) for the A_1 transformation have however been represented by only one line." The writer refers Esser and Cornelius to a statement in our first paper (p. 647) as follows:

The change corresponding to the A_1 change of the Carpenter and Keeling diagram is indicated as a dotted line P-K in Figs. 6, 7, and 8. This is done since it is not the authors' desire to discuss this transition at the present time. Results of further work will be presented in a subsequent paper. (Thus the A_1 data are considered in detail in our second paper[3].)

6. "The fact that through absorption of hydrogen in iron a second A_3 point can appear, shows that the *allotropy* of iron depends greatly on the degree of purity of the iron." To the writer this seems, as yet, to be a very dubious interpretation. Would it not have been better to state that the *manner*, or *mechanism*, of allotropy depends greatly on the degree of purity of the iron?

Conclusion

Esser and Cornelius conclude as follows: "In view of these experiments one can safely say that the double effect for A_1 and A_3 transformations, observed by Harrington and Wood, is due to their method of preparation of the samples, in which hydrogen must have been absorbed. The discussion of two-step transformations as a property of pure iron and pure iron-carbon alloys is therefore apparently unnecessary."

As we have shown above, we believe that the very excellent research work of Esser and Cornelius establishes quite well just the opposite conclusion, namely; that hydrogen probably was *not* the cause of the doubling observed in our work. We do not believe that the theory developed in our previous papers can be so lightly dismissed, especially since there is such a great deal of corroboratory evidence, other than doubled allotropy, from work of many other investigators. This is carefully described in detail in our second paper[3]. To those who may be interested in discussion of this phenomenon the writer respectfully suggests that they read the previous two papers by Harrington and Wood and, after then reading the paper by Esser and Cornelius, draw their own conclusions.

That doubling of A_3 and A_1 does occur in some ordinarily pure iron and pure iron-carbon alloys as well as in commercial alloys has been definitely established and renders a workable theory one of considerable importance. The status of allotropy in absolutely pure iron remains as a matter of interpolation and hypothesis.

FATIGUE AND THE HARDENING OF STEELS

By Herbert J. French

Prefatory Abstract

An appraisal of the processes of martensitization and age hardening is given in terms of the resistance of steels to fatigue.

Delayed fractures (after 10 million stress repetitions) in martensitized steels are discussed in relation to fatigue testing technique and the utilization of hardened and slightly tempered steels. Methods are given for determining "probable damage lines," that is, the ranges of overstress within which damage should not occur.

Hard martensites are shown to require appreciable proportions of retained austenite, or decomposition products, for high resistance to fatigue. The fatigue limits produced by age hardening copper-silicon and nickel-aluminum steels, at around 400 Brinell, were approximately the equivalent of those of martensitized and tempered steels at the same hardness but their resistance to occasional overstress was not so good.

Strengthening on overstressing in fatigue tests, reported occasionally by earlier investigators, was observed in temper-brittle nickel-silicon steels. Evidence is presented in support of the hypothesis that strengthening by overstressing or initially high ratios of fatigue limit to tensile strength were the result of aging effects, that is, the decay of supersaturated solid solutions initiated by slip. Particle deposition in the slip bands was conceived to obstruct slip and so to improve the resistance to fatigue.

Introduction

SINCE 1925 it has been the custom to set apart an hour annually in memory of a distinguished member of this society, Edward De Mille Campbell. Among Professor Campbell's varied professional activities, which have already been discussed by some of my predecessors who knew him well, was a keen interest in the constitution and hardening of steels. This appeared from time to time in his

This is the eighth Edward De Mille Campbell Memorial Lecture, presented by Herbert J. French, in charge, alloy steel and iron development, The International Nickel Co., Inc., 67 Wall St., New York. The lecture was presented at the Fifteenth Annual Convention of the society in Detroit, October 4, 1933.

writings and is already known to many of you. In particular, his attention was often centered upon the relation between the constitution and the properties of hardened steels and he made a number of important contributions to our knowledge of the subject. It would, therefore, seem to be fitting to devote this hour to a re-examination or appraisal of the processes of hardening in terms of some of the properties produced in steels.

During Professor Campbell's lifetime the processes of martensitization comprised the principal means for securing high hardness and associated properties in steels by thermal treatment. Since that time the nitriding process was developed by Fry[1] and continued study has made it apparent that iron and steels, by additions of a variety of metals or metallic compounds, may be made susceptible to so-called age hardening or dispersion hardening phenomena and by such means may acquire a high degree of hardness.

The Fry nitriding process hardens only the marginal layers of steel articles and is applicable only in special cases. Attention will, therefore, be restricted to the processes of martensitization and age hardening.

General Considerations on Fatigue[2] of Metals

The important position occupied by hardened steels in our present civilization is, as is well known, not solely the result of high hardness and static strength but is due in no small part to their ability to withstand repeated stressing without failure or damage. Mention need only be made of a few applications such as springs, gears, bearings, shafting and battering tools of various types to show the importance to industry of the resistance of hardened steels to what, commonly, has been called fatigue. Since repeatedly applied stresses usually also comprise a searching method of appraisal of the quality of metals, the resistance of steels to repeated stress will be made the principal basis of evaluation in this discussion of the processes of hardening.

The fatigue limit of a metal may be defined as that stress below which fracture will not occur if the metal is subjected to an infinitely large number of repetitions of stress. In general, steels

[1]U. S. Patents, 1,487,584 and 1,649,398: See also the Nitriding Symposium, Transactions, American Society for Steel Treating, Vol. 16, 1929, Special Section, p. 1.

[2]The word "fatigue" does not define the method of failure of metals under repeatedly applied stresses but it has come into common usage and will be employed throughout this discussion.

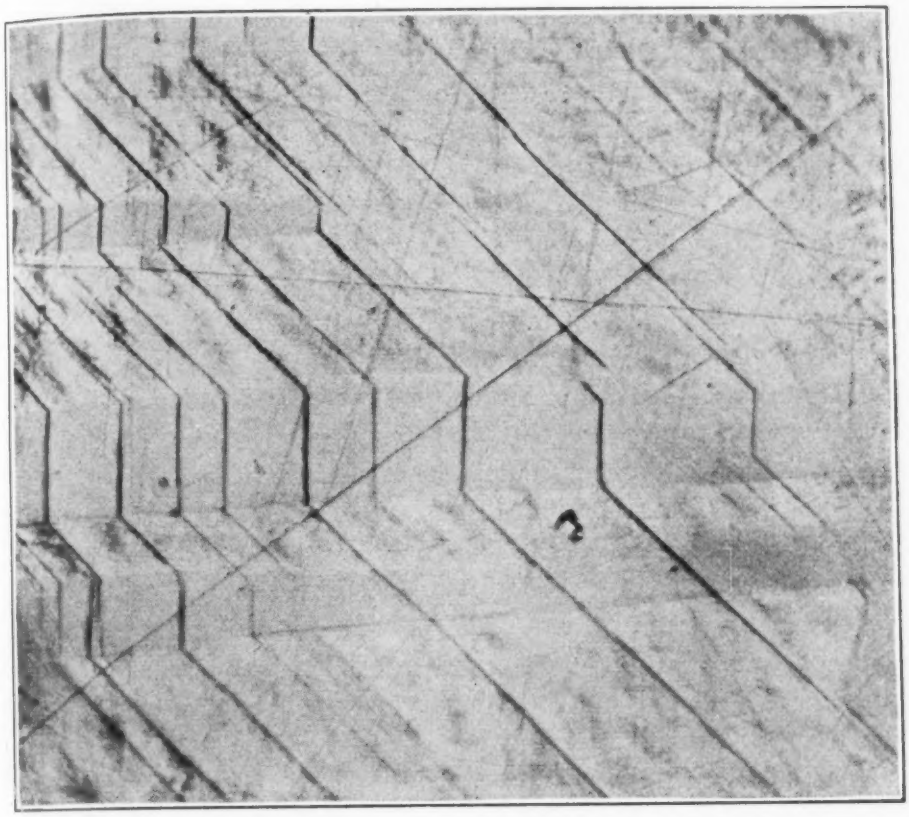


Fig. 1—Slip Bands in Copper. × 1400 (After H. J. Gough).

have well defined fatigue limits which usually are found at 35 to 55 per cent of their tensile strengths. This applies both to carbon and alloy steels at hardness below about 450 Brinell. At higher hardness, the fatigue limits, and hence the ratios between the fatigue limit and the tensile strength are somewhat in doubt.

A complete theory of fatigue is not yet available but certain observations on the behavior of metals when subjected to repeated stresses are enlightening and useful as a prelude to the consideration of the fatigue resistance of hardened steels.

Slip

When a ductile metal is subjected to repeated applications of comparatively high stresses slip bands or slip lines form which are visible under the microscope and which are taken to indicate localized plastic flow. Slip bands in copper, after Gough,[3] are shown in

[3]H. J. Gough, "The Fatigue of Metals," 1924, Scott, Greenwood & Son, London.

Fig. 1. With continued applications of stress one or more cracks form which progress across the section and ultimately result in fracture.

Slip bands are most readily developed at high stresses, but they have also been observed in a variety of metals by Gough and Hanson[4] after a large number of repetitions of stresses considerably below the fatigue limit. Therefore, visible slip does not necessarily connote impending fatigue failure.

Conversely, an absence of visible slip is no indication of freedom from damage since fatigue failure has been observed in Monel Metal and hard steels by Moore and Jasper[5] from stresses below those required to produce slip, as determined by rise of temperature in repeated stress tests, proportional elastic limit, etc.

Slip involves alteration of the initial atomic bonding and it would be expected to occur first in crystals having the least favorable orientation with respect to the applied stresses or in those of relatively low "strength" in heterogeneous materials. If, upon slip, new bonds of equal or greater strength are formed no damage or a localized strengthening of the structure may be expected. Without such new or improved atomic bonds damage is conceived to occur.

In the usual polycrystalline metal specimens with crystals having different orientations and frequently also differences in composition there is probably an irregular distribution of stress. When slip takes place in a crystal a redistribution of the stress is conceived to occur which can then cause slip in other crystals. These changes can proceed upon continued repetitions of stress until a complete readjustment has been effected. If the new atomic bonds are substantially as strong as the original, the metal should withstand an infinitely large number of stress cycles without damage or failure; if the new bonds are stronger, the resistance to fatigue may be improved whereas if bonds are broken by slip without repair one or more cracks may be expected to form and fracture results.

This visualization of the part played by slip is consistent with the experimental observations on damage by overstressing and strengthening by the repeated application of stresses just below the fatigue limit. This latter effect is called strengthening by understressing and the magnitude of such effects appears to vary in dif-

[4]Gough and Hanson, "The Behavior of Metals Subjected to Repeated Stresses," *Proceedings*, Royal Society, Vol. 104A, 1923, p. 538.

[5]An Investigation of the Fatigue of Metals, University of Illinois, Engineering Experiment Station, Bulletin 142, 1924, p. 22.

ferent metals; the strengthening is generally the most marked when the stress is only slightly below the fatigue limit and a very large number of repetitions made.

Evidence of strengthening by understressing is readily secured by first subjecting a specimen to a large number of repetitions of stress just below the fatigue limit and then raising the stress and determining the life. If strengthening has occurred, the life at the new stress will exceed that of the virgin steel subjected to the same stress.

Strengthening by overstressing has also been observed in ductile steels by Smith[6] and by Aders[7] but the reasons for such effects have been obscure.

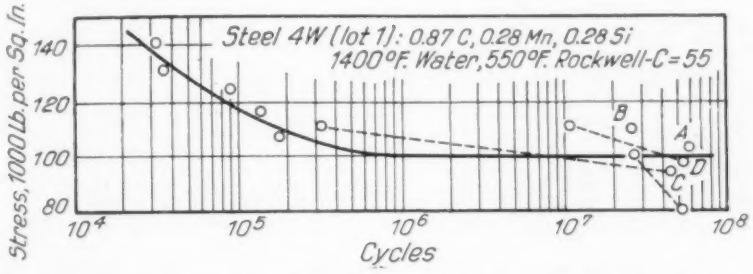


Fig. 2—Life of Quenched and Tempered 0.87 Per Cent Carbon Steel Under Repeated (Reversed Bending) Stress, Showing "Delayed Fractures" (A and B) and Strengthening by Understressing (C and D). Ratio of Fatigue Limit to Tensile Strength = 38 Per Cent.

Until evidence to the contrary becomes available, the fatigue limit may be conceived to represent the stress at which the tendency for damage is exactly balanced by the strengthening from understressing.

Delayed Fractures in Hardened Steels

The determination of the fatigue limit of ductile steels is generally considered to require tests not exceeding 10 million cycles since it has been shown that a specimen which will withstand this large number of repetitions of stress without fracture will withstand many more and, presumably, an infinitely large number.

This point of view must be modified when considering hardened steels or those hardened and slightly tempered since specimens which did not fail in tests run to 10 million cycles of stress some-

[6] J. H. Smith, "Some Experiments on Fatigue of Metals," *Journal*, Iron and Steel Institute, 1910, Part II, p. 246.

[7] K. Aders, "Influence of Aging on the Endurance of Soft Steel," Mitt. a.d. Forschungsinstitut der Vereinigte Stahlwerke A. G. Dortmund 1, 1928-1930, p. 201.

times failed suddenly after 30 to 60 million repetitions. This is illustrated in Fig. 2 and makes necessary a somewhat more tedious testing technique than is required with ductile steels for an accurate determination of the fatigue limit.

These tests and those used as the basis for subsequent discussion were made at speeds of 1750 or 3450 revolutions per minute on R.R. Moore rotating beam machines. Polished specimens of the form and dimensions shown in Fig. 3 were used which could be hardened throughout their effective sections both in shallow hardening carbon steels and deep hardening alloy steels. A majority of

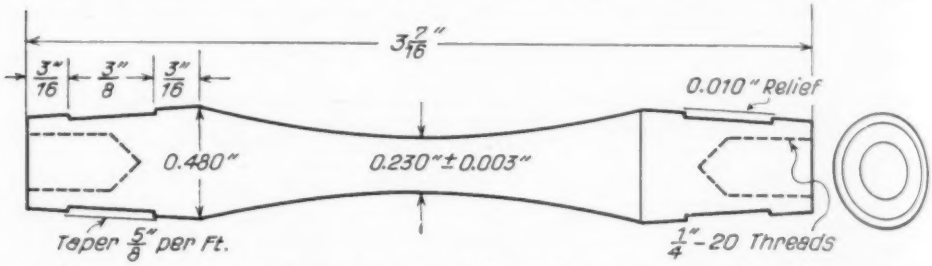


Fig. 3—Form and Dimensions of the Polished Test Specimens Used in the Reversed Bending (Fatigue) Tests of Hard Steels.

the tests were extended well beyond 10 million repetitions of stress and if fracture did not occur in from 30 to 60 million or more cycles the stress was raised, as is indicated by the dotted lines in the graphs, and the life at the higher stress determined and compared with the life of virgin specimens at the same stress. In this way damage at the original stress, or strengthening by understressing, were determined and the fatigue limit more accurately located. Examples of delayed fracture are shown at A and B in Fig. 2; strengthening by understressing is shown at C and D. The fatigue limit must obviously be at a stress close to, but above D, since strengthening was observed, but it must also be below the stress for A which broke after 59 million cycles.

It is interesting to note from Table I that delayed fractures—those well beyond 10 million cycles—were prevalent both in the quenched steels, not tempered, and in those tempered at 550 and 675 degrees Fahr. after hardening. They were not, however, encountered at all in the same steels tempered at 750 degrees Fahr. (spring temper) or higher temperatures. The dividing line, in terms of hardness, appears to be somewhere between 45 and 50 on the Rockwell "C" scale. Delayed fractures were observed at hardness above this range but not below.

Table I
Effect of Tempering on Delayed Fractures in Rotating Beam Fatigue Tests of Hardened Steels[1]

Treatment	Rockwell "C" Hardness	No. of Tests Run Beyond 10 Million Cycles	Fractures Beyond 10 Million Cycles	
			Number	Life at Fracture, Millions
Quenched, not tempered	59/63	15	9	18/52
Quenched, tempered 550/675° F.	51/55	27	12	16/59
Quenched, tempered 750/800° F.	44/45	6	0	.....

[1]The following steels, heat treated as indicated, were included in the tests: 0.87 C, water; 0.75 C, 3.1 Ni, oil; 0.72 C, 2.1 Ni, 0.3 Mo, oil; 0.56 C, 2.1 Ni, 0.3 Mo, oil; 0.50 C, 3.0 Ni, 1.6 Si, oil.

Speculation on why tempered steels show delayed fractures may be useful in emphasizing the importance of these effects both as regards fatigue testing technique and the utilization of hardened and slightly tempered steels.

Tempering at around 550 to 675 degrees Fahr. provides increased atomic mobility for stress readjustment in martensitized steels. Any austenite retained on quenching should be largely if not wholly decomposed and there is also at least a partial decomposition of the martensite. The resulting troosto-martensitic structure, both in high carbon and medium high carbon steels, is essentially ferrite with the carbide in a finely divided and unstable state; it has, as will be shown later, a high fatigue limit and a high resistance to overstress, characteristics which indicate a high resistance to slip both from the standpoint of stress intensity and the number of repetitions.

But such a structure will not undergo appreciable deformation before rupture takes place. This lack of ductility of the crystalline aggregate is probably a reflection of the characteristics of the crystal lattice since when deformed at ordinary atmospheric temperatures fracture in polycrystalline steel specimens is transcrystalline and not intercrystalline. When subjected to a large enough number of repetitions to break some of the initial atomic bonds, new ones of equal or greater strength cannot be expected so readily to develop as in more ductile steels.

Determination of the Effects of Overstress

The information secured from the usual stress-cycle graphs is useful but there are many classes of service in which steels are sub-

jected at least occasionally to overstress. It is, therefore, profitable to expand the usual testing technique, comprising the measurement of life at different ranges of repeated stress, to include studies of the damage from overstress.

Subsequent to the determination of the usual stress-cycle graphs, specimens may be subjected to a range of repetitions of overstress and then tested at the fatigue limit to ascertain whether or not damage resulted. If fracture of the overstressed metal does not occur in 10 million or more cycles at the original fatigue limit the stress may again be raised and the life determined for comparison with that obtained on the virgin metal.

The results obtained by such methods of test may be summarized in several ways. In Fig. 4 the solid circles represent the

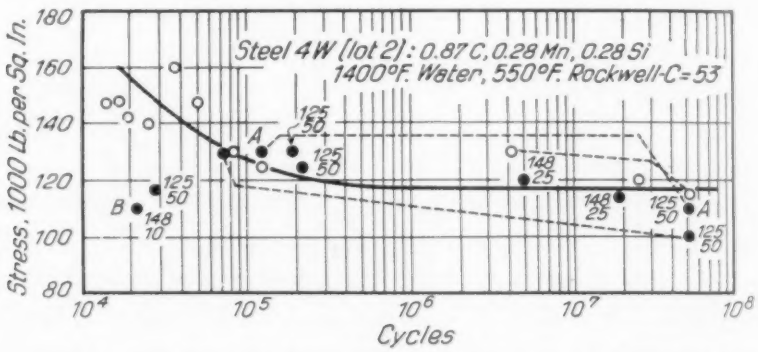


Fig. 4—Effects of Overstress Upon the Life of Quenched and Tempered 0.87 Per Cent Carbon Steel Under Repeated Stress. Hollow Circles Define the Stress-Cycle Curve for the Virgin Metal. Solid Circles are Placed at Positions Indicating Stress and Life After the Preliminary Overstress, Which is Indicated by the Numbers Adjacent to the Points. The Upper Number Represents the Overstress in Thousand Pounds Per Square Inch, the Lower, the Repetitions in Thousands. Ratio of Fatigue Limit to Tensile Strength Equals 44 Per Cent.

results obtained on the overstressed steel.[8] The magnitude and duration of the overstress are indicated by the figures adjacent to the individual points, the values of the overstress in thousand pounds per square inch being placed above the number of repetitions in thousands. Where fractures did not occur in 10 million or more cycles and the stress was raised the points on the chart are connected by dotted lines.

[8]This stress cycle curve differs from that of Fig. 2 for the same steel and treatment. The origin of the differences in the two sets of specimens, heat treated at different times, is not known but attention is called to Figure 9 showing that the fatigue resistance of the steel under discussion is highly susceptible to small variations in heat treatment, especially at low temperature tempering. Four independent sets of determinations gave fatigue limits of 100,000, 118,000, 122,000, 110,000 pounds per square inch, respectively, and an average of 113,000 pounds per square inch.

The sample represented by the points marked A in Fig. 4 was subjected to overstress at 125,000 pounds per square inch for 50,000 cycles (indicated by the numbers adjacent to the point), then tested at 110,000 pounds per square inch and did not fracture in 50 million cycles. The stress was next raised to 130,000 pounds per square inch and a life of about 120,000 cycles obtained. This life, within the scatter of points ordinarily shown in the results of repeated stress tests, is equal to that obtained in the virgin metal at a similar stress and shows that no damage resulted from the overstressing. Overstress at 148,000 pounds per square inch for 10,000 cycles damaged a duplicate sample, represented by point B in Fig. 4 since, when subsequently tested at a stress below the fatigue limit where its life should have been infinitely long, it failed in about 22,000 cycles.

Another method of summarizing the effects of overstress, and one which probably gives a more useful picture for some purposes,

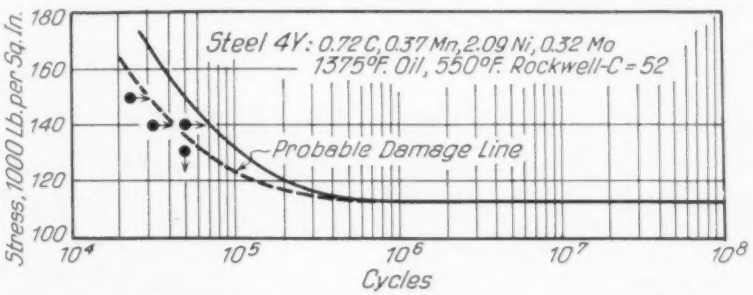


Fig. 5—Effects of Overstress Upon the Life of Quenched and Tempered Nickel-Molybdenum Steel. Solid Circles are Placed at Positions Defining the Conditions of Overstress. Horizontal Arrows Attached to these Points Indicate no Damage as Determined in Subsequent Tests at the Fatigue Limit of the Virgin Metal or at Higher Stresses. Arrows Pointing Downward Indicate Damage, those Pointing Upward (None Shown) Improvement. Ratio of Fatigue Limit to Tensile Strength = 37 Per Cent.

is illustrated in Fig. 5. Here the solid circles are placed at positions defining the conditions of overstress. Adjacent arrows which point downward indicate damage as determined in subsequent tests at the fatigue limit of the virgin metal or at higher stresses. Horizontal arrows indicate no change while arrows pointing upward (none shown) may be used to designate improvement in fatigue resistance.

With two notable exceptions, which will be discussed later, overstress resulted either in no detectable effects or clear evidence of damage and Fig. 5 may be considered to be representative of the character of the results obtained in a variety of steels quenched or quenched and tempered to give hardness values at or above about 440 Brinell.

A line may be drawn in the stress-cycle graph, as in Fig. 5, to indicate the boundary at which damage is liable to occur. Such "damage lines" are, of course, approximate and can only be accurate if enough overstress tests are made to establish their form. The area below the damage line represents the safe stress-cycle range since it defines approximately the number of repetitions of different stresses within which the material remains unimpaired. When the area under the damage line is large the metal may be said to have a good resistance to overstress while when small, damage from overstress can be said to be more readily produced.

There is a scatter of points in the determination of the damage line just as there is in that of the stress-cycle curve for the virgin metal. The damage line must, of course, join the stress-cycle curve of the virgin metal at the fatigue limit since by definition this is the limiting stress below which an infinitely large number of repetitions may be applied without failure and therefore without damage. As the stress range is increased the cycles required to produce damage decrease.

Tests on a variety of steels treated in different ways indicated that the damage line was often, though not invariably, similar in form, and not far below, the stress-cycle graph for the virgin metal. Steels with comparatively long life at stresses well above the fatigue limit usually, though not invariably, showed high resistance to damage. Expressed in other terms the damage line for hard (martensitized) steels followed closely the high stress end of the stress-cycle graph for the virgin metal, an indication that once damage occurs fracture soon results.

Fatigue Resistance of Martensitized High Carbon Steels, Not Tempered

When high hardness is procured through martensitization of unalloyed high carbon steels, water quenching or more rapid cooling is required. More moderate cooling speeds, as in oil quenching, are effective with alloy steels in which the rates of decomposition of the austenite have been lowered and, therefore, the critical cooling speeds reduced, by the addition of the special elements.

The fatigue resistance of these two classes of steels, quenched appropriately to secure high hardness, and not tempered, may vary over rather wide limits. This may be illustrated by the comparisons given in Table II where it is shown that the oil-quenched alloy steels

Table II
Fatigue Resistance of Water-Quenched Carbon Tool Steel and Oil-Quenched High Carbon Alloy Steels

No.	Composition, Per Cent				Quenched		McQuaid-Ehn Grain Size	Vickers-Brinell Hardness	Stress, Lbs. per Sq. In. For Life of Approx. 50,000 Cycles	Stress, Lbs. per Sq. In. At Fatigue Limit
	C	Mn	Ni	Mo	From	In				
4W	0.87	0.28	....	....	1400	Water	6 to 7	705	80,000	72,000
4X	0.75	0.32	3.08	....	1340	Oil	5 to 6	685	135,000	100,000
4Y	0.72	0.37	2.09	0.32	1375	Oil	7	840	150,000	92,000
4Z	0.56	0.36	2.07	0.29	1425	Oil	7	710	125,000	92,000

have higher fatigue limits and also better resistance to overstress than the water-quenched carbon steel. The magnitude of these differences is, perhaps, portrayed more strikingly in Fig. 6 where the

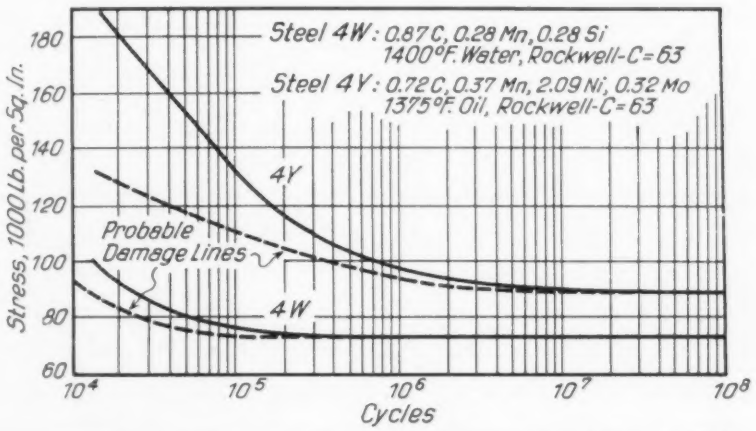


Fig. 6—Resistance to Fatigue (in Reversed Bending) of High Carbon Steel Water-Quenched, and High Carbon Nickel-Molybdenum Steel, Oil-Quenched. Probable Damage Lines on Overstress were Determined by Methods Described in the Text.

stress-cycle curves and probable damage lines are given for the water-quenched carbon steel containing 0.87 per cent carbon and the oil-quenched nickel-molybdenum steel containing 0.72 per cent carbon, about 2 per cent nickel and 0.3 per cent molybdenum. Plotting of individual points has been omitted for simplification.

The superiority in the resistance to fatigue of the alloy steels over quenched carbon steels in the same high hardness range may be conceived to result in part from the strengthening of the martensite by the added alloying elements but it is probably associated also with differences in residual stress. The nature of these stress variations is not readily determined but certain observations throw

light on the probable origin of the differences and tend to support the view that internal stress plays a most important role.

When the water-quenched carbon steel was tempered at about 550 degrees Fahr. the fatigue limit and the resistance to overstress were markedly increased as is shown in Fig. 7. With increase in

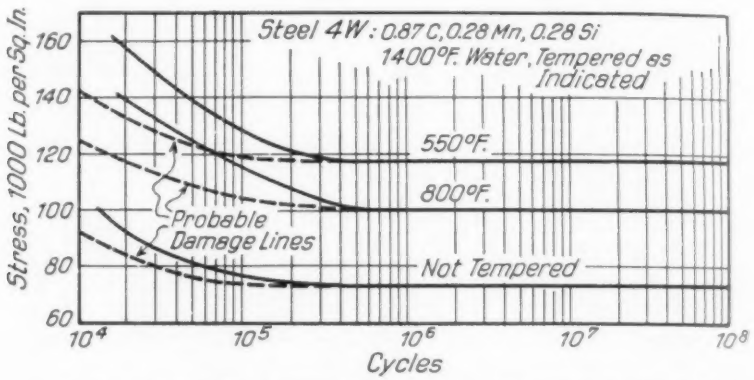


Fig. 7—Effects of Tempering Upon the Resistance to Fatigue of Water-Quenched 0.87 Per Cent Carbon Steel. Ratios of Fatigue Limit to Tensile Strength are: 44 Per Cent When Tempered at 550 Degrees Fahr. 50 Per Cent When Tempered at 800 Degrees Fahr.

the tempering temperature from 550 to 800 degrees Fahr. the fatigue resistance was lowered but it did not reach the low values of the quenched steel, not tempered.

The stresses generated by the volume changes in hardening are at least partially relieved by the tempering at 550 degrees Fahr. which raised the fatigue limit more than 35 per cent, from 72,000 pounds per square inch to an average of about 113,000 pounds per square inch in four separate sets of tests. Stress relief from increased atomic mobility is not, however, the only effect induced by the tempering. Structural changes occur comprising decomposition of retained austenite into alpha iron and carbide and, in addition, a partial tempering of the martensite. The fatigue resistance might be improved directly by these structural changes apart from their influence on the redistribution of stress.

The importance of stress is, perhaps, somewhat better developed by considering the effects of martensitization at liquid air temperatures on the fatigue resistance of steels which retain an appreciable percentage of austenite on quenching. The conversion of the retained austenite to martensite at low temperatures can provide steel with practically a complete martensitic structure and should favor stress generation since the volume increase accompanying the trans-

formation occurs under conditions of low atomic mobility. If the redistribution or relief of stress was largely responsible for the improvement in fatigue resistance of the carbon steel on tempering, martensitization of the retained austenite in an alloy steel at low temperatures might be expected to reduce the resistance to fatigue.

Tests made on an oil-quenched steel containing about 0.75 per cent carbon and 3 per cent nickel with a retained austenite content of 6.4 per cent showed a fatigue limit of about 100,000 pounds per square inch. Upon conversion of the austenite to martensite at liquid air temperatures the fatigue limit was lowered about 20 per cent to approximately 79,000 pounds per square inch, a value which is of the same general order as that of the fatigue limit of water-quenched carbon steels with high carbon contents and about 3 per cent or less of austenite.

The amount of austenite retained on quenching was determined by magnetic test methods. Those used comprised a modification of methods described by Maurer and Schroeter[9] and by Tamaru and Sekito.[10]

Two similar cylindrical specimens about 0.3 inch in diameter were nicely fitted between parallel poles on an electromagnet. Coils around these specimens, connected to a ballistic galvanometer, permitted determination of the magnetic properties. A similar coil in air determined the field strength. Relatively small changes in the properties of one specimen were determined by comparing it with the other one maintained as a standard.

The ferric induction of one of the specimens was determined at a field strength nearly sufficient to cause saturation (about 830 oersteds)[11] and maintained at the selected value. One of the pair of specimens was then immersed in liquid oxygen (—310 degrees Fahr.) for 30 minutes. The resulting change in ferric induction was then measured using the ballistic galvanometer in a sensitive condition and a circuit which gave a deflection proportional to this change rather than proportional to the total ferric induction. This change divided by the new ferric induction gave the amount of transformed austenite expressed as a fraction of the whole amount of iron. Suc-

[9]Stahl und Eisen, Vol. 49, 1929, p. 929.

[10]Science Reports, Tohoku Imperial University, Vol. 20, 1931, p. 377.

[11]According to the results obtained by Tamaru and Sekito the amount of retained austenite, determined by the method described, is substantially the same as that determined at saturation.

cessive liquid oxygen treatments were given until no further changes were indicated.

The percentages of retained austenite indicated by this method may be somewhat lower than those actually present due to incomplete conversion of gamma to alpha iron at liquid air temperatures at which atomic mobility is low. They should, therefore, be considered to represent only comparative values until confirmed by other methods of test.

The Role of Austenite in Quenched Steels

Additional evidence of the importance of retained austenite is given by a comparison of the fatigue resistance of oil-quenched and water-quenched nickel-molybdenum steels containing about 0.7 per cent carbon, 2 per cent nickel and 0.3 per cent molybdenum.

According to Mathews[12] the water-quenched samples should have less retained austenite than those quenched in oil. Determinations by the method already described showed a retained austenite of 4.8 per cent in the oil-quenched steel and less than one-tenth this amount, about 0.4 per cent, in the water-quenched samples.

As is shown in Table III, the water-quenched steel with the

Table III
Fatigue Resistance and Retained Austenite in Water-Quenched and Oil-Quenched Nickel-Molybdenum Steel

(Melt 4Y—0.72 Per Cent Carbon, 2.1 Per Cent Nickel, 0.3 Per Cent Molybdenum)

Quenched		Retained Austenite, Per Cent	Fatigue Limit, Lbs. Per Sq. In.
From, Degrees Fahr.	Into		
1375	Oil	4.8	92,000
1375	Water	0.44	80,000

lesser amount of austenite had a lower fatigue limit than the oil-quenched samples of the same steel. It should also be noted that the fatigue limit of about 80,000 pounds per square inch in the water-quenched nickel-molybdenum steel is somewhat higher but of the same general order of magnitude as that of 72/76,000 pounds per square inch found for water-quenched carbon steels.

Correlation of the retained austenite with the fatigue limits of a variety of quenched high carbon steels is given by the hollow circles in Fig. 8 and shows that the role of austenite may be an im-

[12] J. A. Mathews, "Retained Austenite—A Contribution to the Metallurgy of Magnetism," TRANSACTIONS, American Society for Steel Treating, Vol. 8, 1925, p. 565.

portant one. With less than 3 or 4 per cent retained austenite, as determined by the magnetic test method described, the fatigue resistance was relatively poor. With the retention of about 5 per cent or more of austenite an appreciable improvement was secured in the

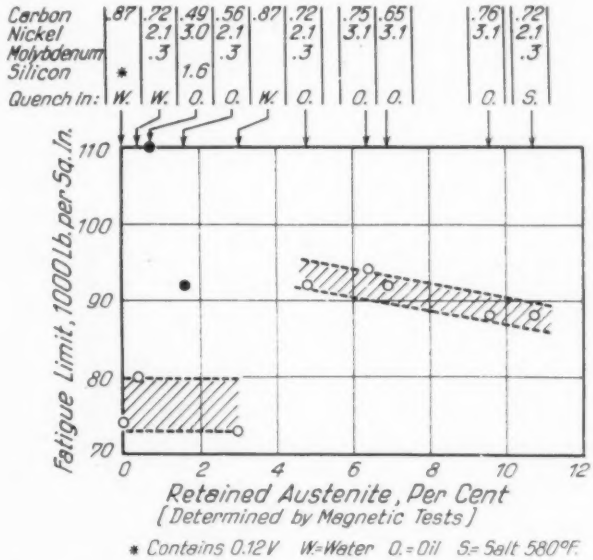


Fig. 8—Effect of Retained Austenite on the Fatigue Limit (in Reversed Bending) of Quenched Steels. Hollow Circles Represent Steels Which Gave Hard Martensites on Quenching, Solid Circles, Steels Which Did Not. See Text for Discussion.

fatigue limit. While not shown in Fig. 8 there was also a greatly improved resistance to overstress.

Austenitic alloy steels, whether low or high in carbon, are characterized by relatively low elastic properties and hardness. Their tensile strengths, as is shown in Table IV, are frequently below, and seldom exceed, about 100,000 pounds per square inch without cold

Table IV
Approximate Tensile Properties of Austenitic Alloy Steels

Approx. Composition, Per Cent				Tensile Strength	Yield Point.
C	Mn	Ni	Cr	Lbs. Per Sq. In.	Lbs. Per Sq. In.
0.10	..	9	18	85,000	40,000
0.25 max.	..	14	25	100,000	50,000
low	..	36	..	75,000	50,000
0.65 max.*	..	23*	22*	60,000†	40,000†
Eutectoid	12	3.5	..	105,000†	28,000†

*Alloy contains 1.8 Silicon.
†Castings, others wrought steels.

work. Their fatigue limits are probably also low, although generally they have a high capacity for work hardening.

The relatively good fatigue resistance of the oil-quenched high carbon alloy steels is, therefore, probably not due to the introduction of a component of superior mechanical properties but rather to the influence of the austenite on the stress effects of martensitization by quenching or its influence on the strain, i.e., slip during the repeated stress. Indeed there is evidence in Fig. 8 which indicates that increase in the retained austenite from around 5 to 10 per cent in the oil-quenched high carbon alloy steels tends to lower the fatigue limit slightly. It would therefore seem probable that the benefits derived from the austenite are quite largely the result of its role in affecting stress and strain.

Its comparative softness, its ability to deform and the absence of volume increases during cooling would make it possible for austenite to exert a cushioning effect in the process of hardening and later under repeated stress, provided it is distributed rather broadly throughout the metal where it can do the most good.

The alloy steels designated by the hollow circles in Fig. 8 each contain sufficient carbon to provide hard martensite on simple quenching. The role of austenite appears to be much less important in steels with lower carbon contents which, when quenched, were not so hard but more plastic. This is illustrated in Fig. 8 by the solid circles representing a nickel-molybdenum steel with 0.55 per cent carbon and a nickel-silicon steel with about 0.5 per cent carbon. The retained austenite on oil quenching was less than 1¾ per cent in both steels, yet the fatigue limits were higher than that of the water-quenched carbon steel with about twice this proportion (3 per cent) of retained austenite.

The two medium-carbon alloy steels, when oil-quenched, were not so hard as the water-quenched high carbon unalloyed steel, and the highest fatigue limit was shown by the steel giving the lowest hardness, as is shown in Table V.

Table V

Fatigue Limits of Quenched High Carbon Steel and Medium Carbon Alloy Steels, Their Hardness and Retained Austenite

Steel	Quenched In	Retained Austenite Per Cent	Rockwell "C" Hardness	Fatigue Limit Lbs. Per Sq. In.
0.87% C	Water	2.9	64	72,000
0.56% C, 2% Ni, 0.25% Mo	Oil	1.6	60	92,000
0.49% C, 3% Ni, 1.50% Si	Oil	0.7	55	110,000

It would seem reasonable to conclude from these results that martensite of medium high carbon content in quenched steels has better resistance to fatigue than hard high carbon martensite but where the service requirements demand the highest range of hardness high carbon steels which retain from about 5 to 7 per cent of austenite on quenching—that is, alloy steels—are better able to resist fatigue than those steels with about 3 per cent or less of austenite.

In the absence of evidence defining exactly the role of retained austenite in the hardening of steels speculation on the means by which it can improve the fatigue resistance is of interest.

Lucas[13] has shown that martensitized high carbon unalloyed steels contain minute cracks, visible under the microscope at high magnification, in the needle areas. He stated, "if a hardened steel part containing these minute cracks is one which will be subjected to reversed cycles of stress, each little crack becomes potentially the starting point for a fatigue failure."

More recently Bain[14] sought evidence of cracks in hardened steels and concluded that "a correlation was unescapable that brittleness was associated with the minute cracks described by Lucas. When the cracks become very prevalent the specimen was invariably visibly cracked in heat treatment."

Cracks were not found in the very fine-grained steels regardless of the heating temperature for quenching but Bain concluded that the cracks were "not a result alone of the depth of hardening nor dependent solely on the severity of quench."

Cracks of the type under discussion were estimated by Lucas to have a minimum width of the order of 25 atoms and a length of 1000 atoms and with dimensions of this order of magnitude might be expected to have a highly deleterious effect upon the mechanical properties, including the resistance to fatigue, of hardened steels.

As a result of the cushioning effects of retained austenite, already discussed, real or pseudo cracks would be expected to be more prevalent in unalloyed high carbon steels than in the oil hardening alloy steels with their higher proportions of austenite. As is shown in Fig. 9, the fatigue resistance of quenched high carbon steels is improved appreciably by tempering at temperatures in the neighborhood of 550 degrees Fahr. The improvement which occurs is even

[13]F. F. Lucas, "On the Art of Metallography," *Transactions*, American Institute of Mining and Metallurgical Engineers, 1931, Iron and Steel Division, p. 11.

[14]E. C. Bain, "Factors Affecting the Inherent Hardenability of Steel," TRANSACTIONS, American Society for Steel Treating, Vol. XX, Nov. 1932, p. 385.

more marked in steels with small amounts of retained austenite than in those with the larger amounts and this may be interpreted to indicate (1) that the cracks heal on tempering or as a result of a sort of mechanical aging in the repeated stress tests themselves, (2) the cracks are not located at or near the surface in those areas subjected

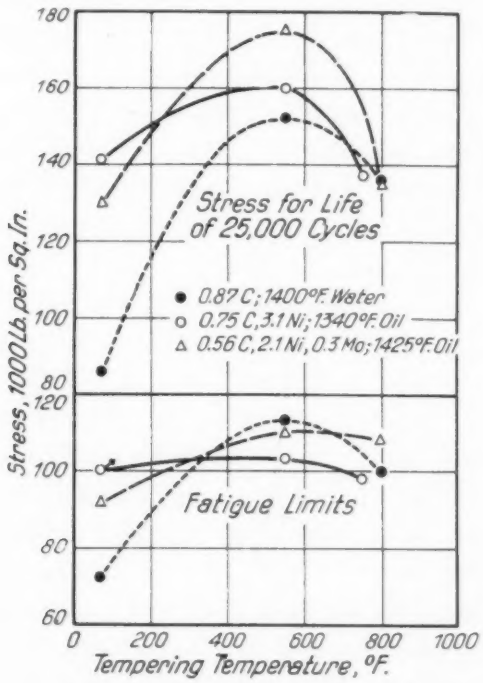


Fig. 9—Effect of Tempering on the Fatigue Resistance (in Reversed Bending) of Martensitized High Carbon Steels.

to the maximum stress in reversed bending tests, (3) that the markings observed in polished and etched sections under the microscope were in the main not originally real cracks—i. e., permanent ruptures of atomic bonds—but rather lines of strain or pseudo cracks.

If the markings are real cracks but do not occur in the marginal areas subjected to the maximum stresses in the reversed bending tests, they might not affect the observed values of the fatigue limit but if the quenched steel was subjected repeatedly to high stresses, well above the fatigue limit, stress concentrations around interior cracks might be expected to restrict the life. The evidence available, however, indicates that unalloyed high carbon steel, with a very short life at stresses above the fatigue limit, when water-quenched, has a very greatly improved resistance to failure at high stresses when tempered after hardening (Fig. 9).

Davenport and Bain[15] have observed markings in the martensite needles of quenched steels which did not heal on reheating until temperatures in excess of about 1900 degrees Fahr. were reached but in other instances the markings disappeared on tempering. They consider that, in general, such markings represent stress concentrations which are reduced or dissipated on tempering and therefore not true ruptures.

But whether the markings observed under the microscope in the martensitic needles represent permanent rupture of atomic bonds prior to preparation for microscopic examination or whether, as seems more probable, they develop in polishing or etching from pseudo cracks, they may be considered to be equally undesirable from the standpoint of the utilization of the hardened steel and they should be prevented whenever practicable.

Bain's observations on the behavior of very fine-grained steels indicate that control of the methods of steel manufacture may be helpful in the elimination of cracks or potential rupture of the atomic bonds. This method has obvious limitations, however, in relation to the depth of hardening procurable.

Quenching in heated liquid baths is another method proposed for avoiding the formation of so-called cracks but this is applicable only where the hardness requirements for the heat treated product are somewhat below that of high carbon martensite. This method either eliminates the formation of martensite entirely or the martensite exists only at elevated temperatures as a stage in the more complete decomposition of the austenite.

It seems probable that the retention of austenite can operate, through alteration in the stresses arising from martensitization, so as to reduce or eliminate real or pseudo cracks and so to improve the mehanical properties and especially the resistance to fatigue of the steel in the manner described. But whether or not this is a correct appraisal of a part of the role of austenite it appears that hard martensites require appreciable proportions of retained austenite for high resistance to fatigue, a condition which is obtained most readily by the introduction into the steel of those special elements which tend to retard the rate of austenite decomposition at low temperatures.

Age Hardening in Iron Alloys

By reason of their almost unique position in being susceptible

[15]Private communication.

to hardening by heat treatment, steels long dominated those fields of application requiring high hardness, high strength or resistance to fatigue. But with increase in our knowledge of so-called age hardening phenomena, many alloys have become known which are hardenable by heat treatment alone and there is no longer so sharp a distinction between the strength and hardness which may be developed in steels and nonferrous metals.

Merica[16] in the Institute of Metals lecture on "The Age Hardening of Metals," given in 1932 before the American Institute of Mining and Metallurgical Engineers, pointed out that—"the hardness of copper may thus (by age hardening) be increased from its value of 35 Brinell in the annealed condition to about 400 in the 2.5 per cent beryllium-copper alloy. The tensile strength of 30 per cent copper-nickel alloys may be increased from 75,000 pounds per square inch to approximately 175,000 pounds per square inch in the 4 per cent aluminum-copper-nickel system. In the less generally known field of precious metals, none of which has a tensile strength over about 35,000 pounds per square inch in the annealed condition, tensile strengths of 175,000 to 200,000 pounds per square inch may be developed."

"In short, strength and hardness values may be developed in many nonferrous alloys comparable with those of heat treated steel, and age hardening alloys are known which develop hardness values equal to those of the hardest steels known."

The conditions which must be fulfilled for age hardening to occur are summarized concisely by Merica as follows: "The alloy must contain a hardening constituent, be it metal or metallic compound, of which the solubility in the base alloy at higher temperatures is greater than at lower ones. The solid solution, saturated at high temperatures with respect to the hardening constituent and rapidly cooled or quenched to lower ones, is, at these temperatures, supersaturated and unstable. During the process of decomposition of this unstable solution, occurring gradually at lower or intermediate temperatures, the alloy age-hardens."

Many details relating to the mechanism of age hardening are unknown but the conceptions given will serve the present purposes and are illustrated graphically in Fig. 10 by part of the equilibrium diagram of copper-iron alloys.

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[16] *Transactions*, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, 99 (1932), p. 13.

It has become evident as a result of continued studies during recent years that iron and iron alloys are susceptible to aging phenomena over a rather broad range of conditions. In fact aging effects which were once believed to be the exception in steels would now rather seem to be the rule.

The manifestations of aging in iron and steel do not always include increases in hardness but a variety of addition agents are

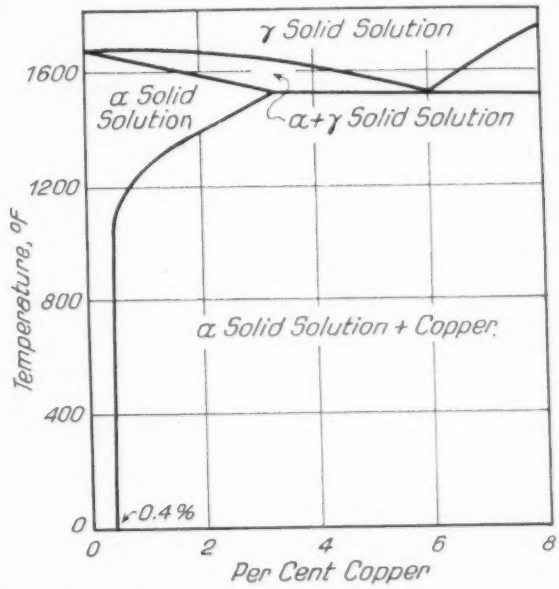


Fig. 10—Solubility of Copper in Iron (After Buchholz and Koster), *Stahl und Eisen*, 1930, 687.

now known which impart age hardening properties to these metals. A partial but representative list of age hardenable iron alloys, their heat treatment and the hardness secured are summarized in Table VI.

A majority of these iron alloys, exclusive of those containing large amounts of tungsten and molybdenum, depend for their age hardening characteristics upon the addition, alone or in combination with other elements, of agents which are readily oxidized in molten steels. Copper is an exception and is interesting also as an illustration of the hardening of a metal by dispersion in it of a much softer one.

While a variety of agents are known which are capable of providing high hardness in iron or steels on aging their hardening ability, in general, is lower than that provided by carbon and the processes of martensitization. This will become evident if the increases in hardness on heat treatment of the alloys listed in Table VI are

Table VI
Partial List of Age Hardenable Iron Alloys, Their Treatment and the Hardness Procured

Iron Alloyed With	Solution Treatment		Brinell Hardness	Aging Treatment		Brinell Hardness	Increase in Brinell Hardness on Aging	Source of Data
	Heat to °F.	Cool In		Heat to °F.	Heat for, Hours			
Tungsten								(1)
20% W	2730	Water	155	1290	2	330	175	
30% W	2730	Water	196	1290	2	456	260	
Molybdenum								(2)
30% Mo	2600	Water	272	1155	20	620	348	
Titanium + Si or Ni								(3)
2% Ti, 2% Si, 0.05% C	1830	Water	195	930	30	390	195	
2% Ti, 2% Si, 0.25% C	1830	Water	195	930	30	375	180	
2% Ti, 2% Si, 0.50% C	1830	Water	210	930	30	210	0	
7.3% Ti, 2% Si	2380	Water	320	930	20	650	360	
4.4% Ti, 12.5% Ni	1740	Probably Water	350	930	12	615	265	
2.3% Ti, 8% Ni, 18% Cr	2280	Water	285	930	5	480	195	
6.2% Ti, 8% Ni, 18% Cr	2280	Water	510	930	4	610	100	
Boron								(4)
0.55% B, 8% Ni, 18% Cr	Hi Temp.	Quench	235	1470	72	435	200	
1.1% B, 8% Ni, 18% Cr	Hi Temp.	Quench	280	1470	10	455	175	
Beryllium								(5)
3.9% Be	2010	Water	263	970	1	467	204	
1.0% Be, 5% Ni	2010	Oil	424	840	1	611	187	
1.0% Be, 10% Ni, 19.8% Cr	1740		360			588	222	
Aluminum + Nickel								(6)
1.5% Al, 3.5% Ni, 0.15% C	1550	Air	156	950	24	321	165	
1.6% Al, 3.7% Ni, 0.55% C	1475	Air	286	950	24	418	132	
Copper								(7)
1.1% Cu, 0.19% C	1590	Air	143	930	4	207	64	
1.0% Cu, 0.45% C	1590	Air	190	930	4	240	50	
Oxygen								(8)
0.06% O_2	1255	Quench	105	Room	14 days	160	55	
Nitrogen								(8)
0.04% N_2	1255	Quench	120	Room	14 days	204	84	
Carbon								(9)
0.07% C	1255	Quench	143	70	28 days	185	42	

(1) Sykes, Trans. A. I. M. E. 76 (1926) 968.
(2) Sykes, Trans. A. S. S. T. 10 (1926) 839.
(3) Wasmuht, Kruppsche Monatshefte, July 1931, 159.
(4) Wasmuht, Trans. A. I. M. E. Iron & Steel Div. 1931, 278.
(5) Kroll, Wiss. Veroeffentlichungen a.d. Siemens Konzern, 8 (1929) 220.
(6) Author.
(7) Smith and Palmer, Paper before A. I. M. E. Feb. 1933.
(8) Eilender and Wasmuht, Archiv. f.d. Eisenhuettenwesen, 3 (1930) 659.
(9) Koster, Archiv. f.d. Eisenhuettenwesen, Feb. 1929, 503.

viewed in the light of the effects of martensitization on carbon tool steels. The latter, with a Brinell hardness of about 200 in the annealed condition will, as is well known, increase some 400 units, to about 600 Brinell, upon water quenching. Increases of this order of magnitude on aging are shown by few of the age hardenable iron

alloys now known, a condition which recalls a statement which appeared in 1926 in one of the last of Professor Campbell's papers[17] as follows: "Of all the elements usually associated with iron, carbon stands in a class by itself as regards the extent to which it enables the metallurgist to control those physical properties which give steel the important position it holds in modern civilization."

In view of these circumstances and the relatively low cost involved in the hardening of iron by additions of carbon and the processes of martensitization, age hardenable iron alloys would be expected to find application only where they can provide properties or performance not obtained in the more commonly used steels. That they do in individual cases is now well known. For example, some of the iron-tungsten and iron-molybdenum alloys described by Sykes[18] are not only hard at atmospheric temperatures but resist softening with increase in temperature much better than martensitized steels of the usual types.

As has been pointed out by Nehl[19] age hardenable iron alloys may be useful where high strength or hardness are desired in sections of appreciable dimensions since, in at least some of such alloys, the solution of the hardening elements or compounds and subsequent decay of the supersaturated solid solutions occur slowly. Since rapid cooling (quenching) is not required there are no large temperature gradients and the effects of size are less important than in the processes of martensitization applied to carbon steels and most low alloy-content steels.

Fatigue Resistance of Age Hardened Steels

At this stage of our knowledge generalizations with respect to the mechanical properties of age hardenable steels or iron alloys would appear to be hazardous. Some of such metals, as will be evident from Table VII, can provide substantially as good tensile properties as martensitized and tempered steels of the usual types but others appear to be deficient in ductility when appraised at equal ten-

[17] E. D. Campbell and H. W. Mohr, "The Specific Resistance and Thermoelectromotive Potential of Some Steels Differing Only in Carbon Content," *Journal*, Iron and Steel Institute, Vol. 113, 1926, p. 375.

[18] W. P. Sykes, "The Iron-tungsten System," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 73, 1926, p. 968; "The Iron-molybdenum System," TRANSACTIONS, American Society for Steel Treating, Vol. 10, 1926, p. 839.

[19] F. Nehl, "On the Mechanical Properties of Copper Steels," *Stahl und Eisen*, 1930, p. 678.

Table VII
Comparison of the Tensile Properties and Hardness of Some Age Hardenable Iron Alloys and Martensitized and Tempered Steels

Composition, %, and Condition	Yield Point lb./in.²	Tensile Strength lb./in.²	Ratio Yield to Tensile	Elong. %	Red. Area, %	Brinell Hardness	Ratio Tensile to Brinell	Source of Data
1 Be, 5 Ni								
Solution Treatment	.....	185,000	..	7	52	425	435	W. Kroll, Wiss. V.d. Siemens Konzern, 8 (1929) 220
Age hardened	.....	259,000	..	3	3	610	425	
S.A.E.-3340								
1425° F. oil, 500° F.	235,000	260,000	90	10	41	485	535	Author
1 Cu								
Solution treatment	39,000	58,000	67	38	74	117	495	C. S. Smith and E. W. Palmer: A. I. M. E. Meeting, Feb. 1933
Age hardened	68,000	82,000	63	27	65	180	455	
S.A.E.-1020								
1600° F. water, 1100°	56,000	83,000	67	25	66	163	510	Author
1 Ti, 0.8 Si, 3 Ni								
Solution treatment	85,300	46,600	88	..	..	190	510	R. Wasmuht, Kruppsche Monatshefte, July 1931, 159
Age hardened	96,500	115,000	84	..	..	230	500	
0.9 Al, 3.6 Ni								
Solution treatment	69,700	92,100	76	37	66.9	163*	565	Author
Age hardened	92,800	110,500	84	25	59.4	220*	500	
S.A.E.-2315								
1500° F. water, 950°	92,000	110,000	84	23	63	240	460	Author

*Conversions from Rockwell "C" hardness (6 Rc = 163; 18.5 Rc = 220).

sile strengths or hardness. Aging is quite generally accompanied by appreciable losses in resistance to impact of notched bars and probably on this account as much as for any other reason has so far been considered to be more of a liability than an asset.

Comparatively little is now known of the fatigue resistance of age hardened steels or iron alloys. Tests reported by Buchholz and Koster[20] on low carbon copper-chromium steels containing about 0.9 per cent copper and 0.4 per cent chromium which are partially summarized in Table VIII, showed high fatigue ratios and indicate that increases in the fatigue limit produced by age hardening may be roughly proportional to those secured with equal increases in tensile strength or hardness in martensitized and tempered steels. But the

[20]H. Buchholz and W. Koster, "On the Age Hardening of Copper Steels," *Stahl und Eisen*, May 1930, 687.

Table VIII
Comparison of the Fatigue Resistance of Age Hardened Copper-chromium Steel With That of Martensitized and Tempered Medium Carbon Steel

	0.18 C, 0.87 Cu, 0.42 Cr		0.37 C Steel
	Solution Treatment	Age Hardened	1550° F., Water Quenched 1050° F., Furnace Cool*
Tensile Strength, lbs. per sq. in.	72,500	84,000	94,200
Fatigue Limit, lbs. per sq. in.	40,000	51,000	45,000
Ratio Fatigue Limit to Tensile Strength, per cent	55	61	48

*Tests reported by D. J. McAdam, Jr.

conclusion should not be drawn that a proportional improvement in fatigue resistance is the rule in this class of metals.

Merica[21] quoting the findings of Moore[22] and McAdam[23] points out that "The fatigue limit of annealed duralumin may increase from 10 to 50 per cent during normal (aging) treatments which induce increases in hardness and strength of 100 per cent"—"This is true also of 4 per cent aluminum-copper-nickel alloy and of the nickel-silicon-copper alloys." He states, "This reminds us of the effect of cold working on fatigue strength, which is also much less effective in increasing fatigue strength than in increasing the yield point and tensile strength of metals and alloys generally. One can hardly escape the conviction that internal stresses are here at work. The latter certainly play a part in preventing the full development of fatigue strength in cold worked metals, as has been indicated by McAdam."[24]

Fatigue tests on a nickel-aluminum steel, which are summarized in Table IX, indicate that high fatigue limits may be obtained in at least some of those iron alloys which are capable of giving high hardness, above 400 Brinell, on aging. The fatigue limit of about 90,000 pounds per square inch is below the maximum values which may be developed in martensitized and tempered steels but it is not low for steel having a hardness of 418 Brinell.

But perhaps the most interesting aspect of these fatigue test

[21]See footnote (16).

[22]R. R. Moore, *Proceedings*, American Society for Testing Materials, Vol. 23, 1923, p. 1076.

[23]D. J. McAdam, Jr., Papers 1506 and 1537, American Institute of Mining and Metallurgical Engineers, 1925 and 1926.

[24]D. J. McAdam, Jr., TRANSACTIONS, American Society for Steel Treating, Vol. 8, 1925, p. 782.

Table IX

Changes in the Fatigue Limit on Age Hardening a Nickel-aluminum Steel and Comparison with Martensitized and Tempered S.A.E. Steel 2340

Properties	.53 C, 3.52 Ni, 1.66 Al, 0.11 Cr		S.A.E.-2340 1450° F. Oil; 600° F. (Bull. Univ. Ill. No. 136, p. 31, Moore and Jasper)
	After Solution Treatment (1475° F., Air)	Age Hardenend (950° F., 24 Hrs.)	
Brinell Hardness	286	418	430
Fatigue Limit, lbs. per sq. in.	70,000	90,000	98,000
Ratio Fatigue Limit to Brinell Hardness	245	215	230

results is found in the resistance of the age hardened steel to overstress. As is shown in the lower half of Fig. 11, the probable damage line, determined by methods already described, is far below the high stress—low cycle end of the stress-cycle graph for the virgin metal. In fact it would seem that the age hardened nickel-aluminum

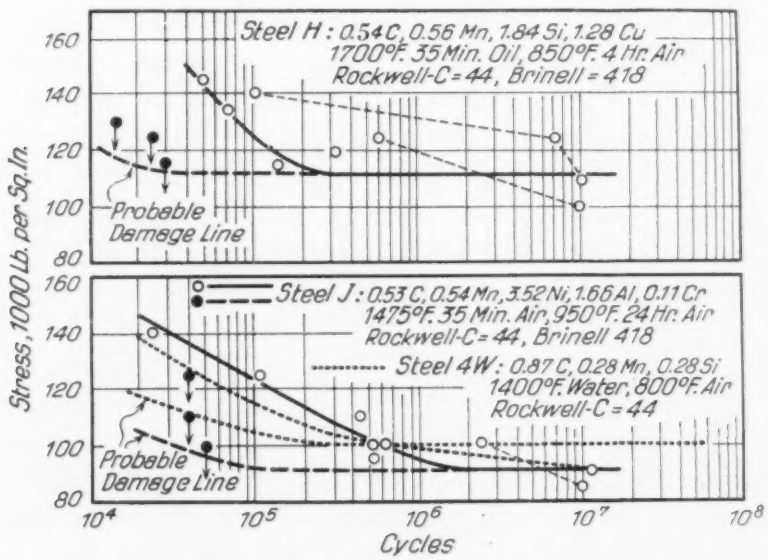


Fig. 11—Stress Cycle Curves and Probable Damage Lines (in Reversed Bending) for Age Hardened Copper-Silicon and Nickel-Aluminum Steels. Data for Martensitized and Tempered 0.87 Per Cent Carbon Steel, at About the Same Hardness, Included for Comparison.

steel could not be subjected to more than a comparatively few repetitions of stress above its fatigue limit without being damaged but after damage occurred there was an appreciable lag before fracture resulted.

The behavior of this steel is not unique since similar effects were observed in a copper-silicon steel, as is shown in the upper half of

Fig. 11. This steel, containing about 0.55 per cent carbon, 0.6 per cent manganese, 1.8 per cent silicon and 1.3 per cent copper, hardens only to about 340 Brinell when aged subsequent to air cooling from high temperatures. The processes of martensitization and age hardening, therefore, were combined to provide the same hardness, of 418 Brinell, as that obtained with the age hardened nickel-aluminum steel. The copper-silicon steel was first oil-quenched from 1700 degrees Fahr. and showed a Brinell hardness of 652; it was then heated for 4 hours at 850 degrees Fahr. for the tempering of the martensite and age hardening.

The question may be raised whether the precipitation of a soft metal like copper could occur in such a matrix as that of the oil-quenched copper-silicon steel, and if it did occur, whether it contributed any hardening effect. That age hardening occurred is suggested by the fact that the same hardness of 418 Brinell was obtained from a short reheating (1 hour) at 750 degrees Fahr. as from the longer heating (4 hours) for aging at the higher temperature of 850 degrees Fahr. Decomposition of the martensite formed on oil quenching should proceed further, and the hardness decrease as the reheating temperature and time are increased. Since the hardness was the same in the two cases some other factor, presumably the age hardening from copper, provided compensation for the more complete tempering of the martensite at the higher temperature.

The copper-silicon steel, like the age hardened nickel-aluminum steel, was readily damaged when stressed above the fatigue limit and, as is shown in Fig. 11, both steels exhibited appreciable strengthening by understressing even at stresses well below the fatigue limit.

Neither the copper-silicon nor the nickel-aluminum steels described show resistance to fatigue quite equal to that which can be developed in martensitized and tempered steels but as a better understanding of age hardenable iron alloys is obtained, and more experience gained, improvement in properties can be expected. But aside from future developments those aspects of the fatigue resistance of age hardened copper-silicon and nickel-aluminum steels, relating to repeated overstress, have been encountered also in martensitized and tempered steels and for this reason become of immediate interest.

Strengthening by Overstressing in Heat Treated Steels

Mention was made previously that strengthening by overstress-

ing had been observed in ductile steels by Smith[25] and by Aders.[26] The results obtained in alternating direct stress tests by Smith on a "rimming" steel are of special interest and are summarized in Table X. Stresses about 17 to 21 per cent above the fatigue limit, but

Table X
Strengthening by Overstressing Observed by Smith* in Low Carbon Steel, Annealed at 1650 Degrees Fahr.†

(0.19, C, 0.60 Mn, 0.02 Si, 0.052 P, 0.047 S)

Overstress		Final Stressing	
Lbs. Per Sq. In.	Cycles	Lbs. Per Sq. In.	Life, Cycles
.....	.....	26,200	183,000
28,600	15,280	26,400	284,520
28,900	30,100	26,400	222,000
29,500	45,720	26,400	97,440
.....	.....	29,100	77,000

*J. H. Smith, Journal I. and S. Inst.; 1910, No. 2, p. 246.
†Fatigue limit, 24,400 lbs. per sq. in., yield point 32,700 lbs. per sq. in., tensile strength 61,500 lbs. per sq. in., Elong. 27.5%, Red. Area, 57.2%, Brinell hardness 121; ratio fatigue limit to tensile strength 39.6%.

under the yield point, were applied 15,000, 30,000 and 45,000 times and the samples then retested at lower stresses and the life determined. After 15,000 and 30,000 repetitions of the overstress the life at a lower stress was improved but after 45,000 repetitions damage appears to have occurred since the life was then less than that obtained on the virgin metal.

Smith stated that similar phenomena had been observed in a number of cases but offered no explanation of the effects. Some fourteen years later Gough[27] in discussing these results and the damaging effects of overstress observed by other investigators on higher carbon steels stated—"We shall see later that the effects of repetitions of an unsafe range of stress upon the crystalline structure can be divided into two stages; during the first stage the crystalline structure of the metal is changed by a process of "slip"; the commencement of the second, and later stage is marked by the formation of actual cracks in the metal. It appears probable that if the action of overstressing be arrested before the "cracking" stage is reached, then no serious effect would be observed on the original fatigue range; in fact, as the process of "slip" is essentially a hard-

[25]See footnote (6).

[26]See footnote (7).

[27]H. J. Gough, "The Fatigue of Metals," 1924, p. 110; Scott, Greenwood & Son, England.

ening process, it appears probable that an *increase* in the fatigue range might result by judicious overstressing."

Studies of the fatigue resistance of martensitized and tempered steels containing medium and high carbon contents revealed no strengthening by overstressing except in the case of a nickel-silicon steel containing about 0.5 per cent carbon, 3 per cent nickel and 1.6 per cent silicon, oil-hardened or hardened and tempered at 675 degreees Fahr.

In these two conditions of treatment this steel showed high resistance to fatigue and the stress-cycle curve for the oil-quenched samples, not tempered, was parallel to, and about 10,000 pounds per square inch above, that of the samples tempered at 675 degrees Fahr. When overstressed in either condition of treatment, the nickel-silicon steel showed evidence of strengthening, as is illustrated in Table XI.

Table XI

Effects of Overstress (in Repeated Bending) on the Fatigue Resistance of Nickel-silicon Steel (Melt 10C). (0.49 C, 3 Ni, 1.6 Si; Oil-quenched from 1575° F.)

Overstress		Final Stress		
Lbs. per Sq. In.	Cycles	Lbs. per Sq. In.	Life, Cycles	Remarks
Not Tempered (fatigue limit = 112,000 lbs. per sq. in.)				
.....	None	130,000	190,000	
137,500	25,000	130,000	810,000	Improved by overstress
.....	None	120,000	1,000,000	
137,500	25,000	120,000	7,600,000	Improved by overstress
Tempered 675° F. (fatigue limit = 100,000 lbs. per sq. in.)				
.....	None	110,000	1,200,000	
125,000	50,000	110,000	10,200,000	Improved by overstress
150,000	25,000	110,000	10,100,000	Improved by overstress

The importance of this effect may be illustrated by comparing the behavior of the nickel-silicon steel with that of overstressed carbon spring steel, at spring temper. Both steels were repeatedly stressed at 125,000 pounds per square inch, equivalent to 125 per cent of their fatigue limits. The carbon steel was subjected to 25,000 cycles and the nickel-silicon steel to from 25,000 to 50,000 cycles. The nickel-silicon steel was also abused more severely by stressing at 150,000 pounds per square inch for 25,000 cycles. The fatigue resistance was then determined as on the virgin metal.

As is shown in Fig. 12, the conditions of overstress which damaged the carbon spring steel improved the fatigue resistance of the nickel-silicon steel. While originally the fatigue limits of the two steels were the same, the overstressed nickel-silicon steel showed a fatigue limit about 30 per cent higher than that of the overstressed carbon spring steel.

It has not been practicable, with the time and facilities available, to determine the origin of strengthening from overstressing in the fatigue tests but the magnitude of these effects in the nickel-silicon steel, Melt 10C, would seem to justify speculation on the causes and a description of some additional experiments relating to such phenomena.

The transition from the first stage of slip to the second stage

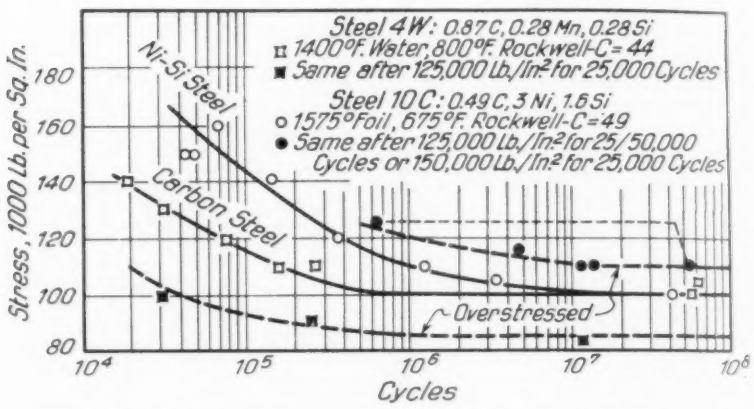


Fig. 12—Effect of Overstressing on the Fatigue Resistance of 0.87 Per Cent Carbon Steel and a Nickel-Silicon Steel.

of crack formation mentioned by Gough[28] might be conceived to progress more gradually in steels with 0.5 per cent carbon, like the nickel-silicon steel, than in high carbon steels which acquire higher hardness when quenched. A low rate of damage might afford an opportunity to observe strengthening from overstressing, but if such was the origin of the described results overstressing could be expected to have brought to light similar effects in other steels softened by tempering at 800 degrees Fahr. or higher temperatures after hardening. The fact that strengthening from overstressing was observed only in one nickel-silicon steel melt suggests that it is peculiar to this steel, in the group considered, and arises from some other source.

Vickers hardness tests made on fatigue test specimens, before and after strengthening by overstressing showed no evidence of hardening nor were any irregularities apparent in the hardness-tempering temperature curves obtained on the nickel-silicon steel as is shown in Fig. 13. Izod tests, however, revealed a sharp drop in the impact energy absorbed when the tempering temperature was raised from

[28]See footnote (27).

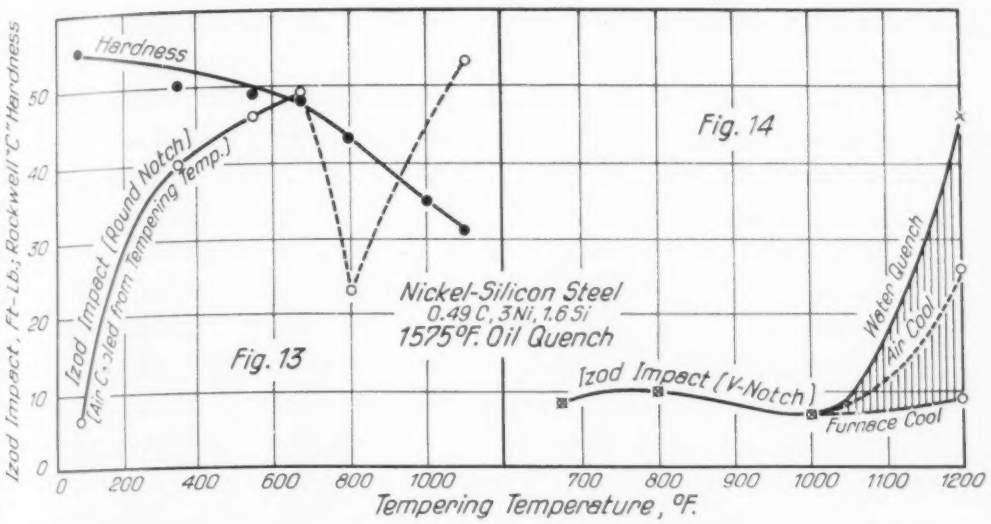


Fig. 13—Effect of Tempering on the Hardness and Impact Resistance of Oil-Hardened Nickel-Silicon Steel (Melt 10 C).
Fig. 14—Susceptibility of Nickel-Silicon Steel, 10 C to Temper Brittleness.

675 to 800 degrees Fahr., with recovery made after tempering at 1100 degrees Fahr.

The tests recorded were made on round bars 0.450 inch in diameter with notches ⅛ inch deep having a radius of ⅛ inch, and the low impact values after tempering at 800 degrees Fahr. were confirmed in four successive sets of experiments.

The usual tests were made for susceptibility to temper brittleness and, as is shown by the summary in Fig. 14, the nickel-silicon steel showed the high susceptibility ratio of 5—that is, the Izod impact values of the samples water quenched from the tempering temperature of 1200 degrees Fahr. were 5 times those obtained on the samples furnace cooled. The fact that the nickel-silicon steel, which was susceptible to temper brittleness was the only one of a large group studied which was strengthened by repeated overstressing in the original fatigue tests suggests that the two phenomena may be related.

Temper brittleness may be considered to represent one type of aging, that is, the decay of a supersaturated solid solution. The results of such decay vary widely in iron alloys. In some cases, as in the copper-silicon and nickel-aluminum steels already discussed, aging is accompanied by marked increases in the hardness while in the temper brittle steels the suspected decay usually is not accompanied by significant changes in the strength or hardness but is

reflected, to the greatest degree, in losses in the resistance to impact of notched bars.

It is not known exactly why such differences exist but they can be conceived to originate from differences in the nature of the solute and solvent, the character of the products of decay and their distribution throughout the steel.

The decay of supersaturated solid solutions postulates particle precipitation which can often be initiated by cold work. Decay may conceivably also be initiated by the slip or localized plastic flow resulting from repeated stressing above the fatigue limit and it might be postulated that deposition of finely dispersed particles in the slip planes can obstruct slip and thereby strengthen the metal.

Aging requires diffusion which, according to the hypothesis suggested, must occur at atmospheric temperatures unless the energy expended in producing slip, being converted into heat, raises the temperature locally at the slip planes by an appreciable amount. Aging at atmospheric temperatures is not unknown in iron,[29] but there is the added assumption that cold work—that is, slip—can *accelerate* the aging.

While this is not known to have been observed in iron alloys Schmid and Wassermann[30] have shown that cold work increases the *rate* of aging of duralumin at atmospheric temperatures and this effect is, therefore, not unknown in metals.

Strengthening from overstressing could, perhaps, originate from other sources, notably as a result of the healing of slip planes, and elastic recovery, produced by heating, but this would seem to be improbable, except under restricted conditions, in view of the results long since reported by Moore and Jasper[31] (summarized in Fig. 15) and others.[32] Axial tensional overstress repeated twenty times at from 15 to 70 per cent above the fatigue limit of sorbitized 0.49 per cent carbon steel, followed by reheating in boiling water, or 3 months aging at atmospheric temperatures, showed no strengthening in the tests made by Moore and Jasper but only damage as the overstress was raised to, and exceeded, the proportional elastic limit.

[29]W. Koster, Archiv. f.d. Eisenhuettenwesen, 1929, 503.

[30]E. Schmid and G. Wassermann, Metallwirtschaft, 1930, 421.

[31]University of Illinois Experiment Station, Bulletin No. 136, 1922, 65.

[32]See for example, references given in The Fatigue of Metals, by H. J. Gough, footnote (27).

Further evidence to support the view that healing and elastic recovery were probably not responsible for the appreciable strengthening by overstressing of the nickel-silicon steel is given by the results of overstress tests on two pairs of specimens of a nickel-molybdenum steel, not susceptible to temper brittleness.

Duplicate specimens of this steel were repeatedly stressed above

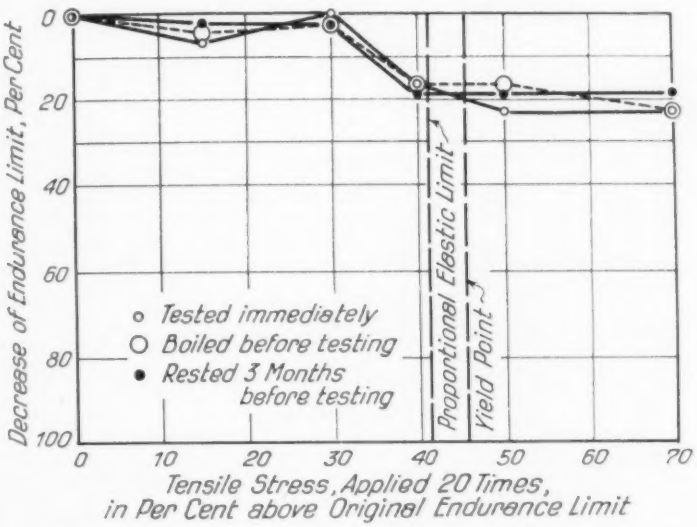


Fig. 15—Diagram Showing Effect on Endurance Limit of Direct Axial Static Stress Applied Twenty Times. (After Moore and Jasper.)

the fatigue limit under conditions which did not produce damage and also for a sufficient number of cycles for damage to occur. One specimen of each pair was then immediately tested at the fatigue limit of the virgin metal (previously determined) and if failure did not occur in 10 million repetitions the stress was raised and the life determined. The second specimen of each pair was tested similarly but only after being heated for 3 hours in oil at 212 degrees Fahr. and cooled. The results of these tests are compared in Fig. 16 with the stress-cycle curves and scatter bands for the virgin metal and it is evident that no appreciable strengthening (i.e, no appreciable improvement in fatigue resistance) was produced either by overstressing or subsequent heating.

While the nickel-silicon steel showed persistent improvement on overstressing when tempered at 675 degrees Fahr., or not tempered at all after hardening, no strengthening was developed by overstressing those samples water-quenched or furnace cooled from a

higher tempering temperature of 1200 degrees Fahr. The resistance to damage at stresses above the fatigue limit was poor after either of these two latter conditions of treatment, and the graphs in Fig. 17 resemble those for the age hardened nickel-aluminum and copper-

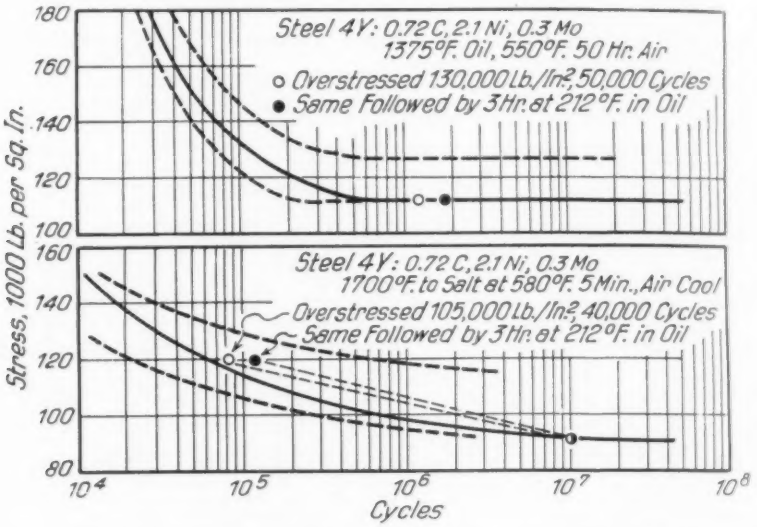


Fig. 16—The Effects of Repeated Overstress and Subsequent Heating of Nickel-Molybdenum Steel in Relation to the Stress Cycle Curves and Approximate Scatter Bands for the Virgin Metal.

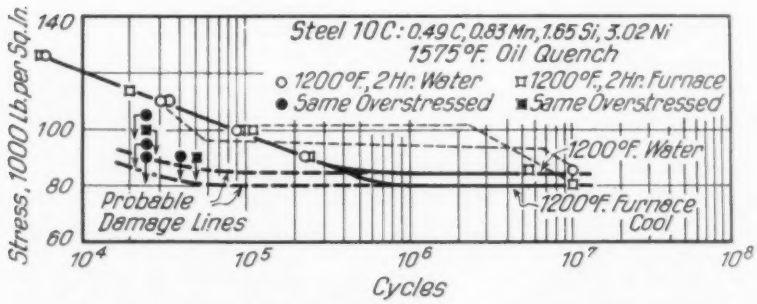


Fig. 17—Effect of Cooling Rate, from a Tempering Temperature of 1200 Degrees Fahr. on the Fatigue Resistance of an Oil-Hardened, Temper Brittle, Nickel-Silicon Steel (Melt 10 C). Ratio of Fatigue Limit to Tensile Strength: 61.5 Per Cent for Water-Quenched Samples. 56.5 Per Cent for Furnace-Cooled Samples.

silicon steels previously described (Fig. 11), both as regards the character of the stress-cycle curves for the virgin metal and the position of the probable damage lines.

There are important differences between the undecayed samples tempered at 1200 degrees Fahr. (then water-quenched) and those tempered at temperatures below the range of decay (675 degrees Fahr.), or not at all after hardening, which might account

for the differences in behavior in overstressing in the fatigue tests.

Attention was called previously to the conception that stress is not uniformly distributed in the usual polycrystalline metal specimens as a result of differences in crystalline orientation, chemical heterogeneity, etc. As is shown in Table XII, the fatigue limit of

Table XII
Proportional Limits and Fatigue Limits of Nickel-silicon Steel, 10-C, Tempered at Different Temperatures

Oil-quenched from 1550 Degrees Fahr. Tempered as Indicated	Prop. Limit, Lbs. per Sq. In.	Fatigue Limit, Lbs. per Sq. In.	Ratio Fatigue Limit to Prop. Limit, Per Cent
675° F. air cool	203,000	100,000	49
1200° F. water quench	110,000	80/85000	73

the nickel-silicon steel samples tempered at 1200 degrees Fahr. (and water-quenched to avoid decay) is much closer to the proportional elastic limit than is the case in the harder samples tempered at only

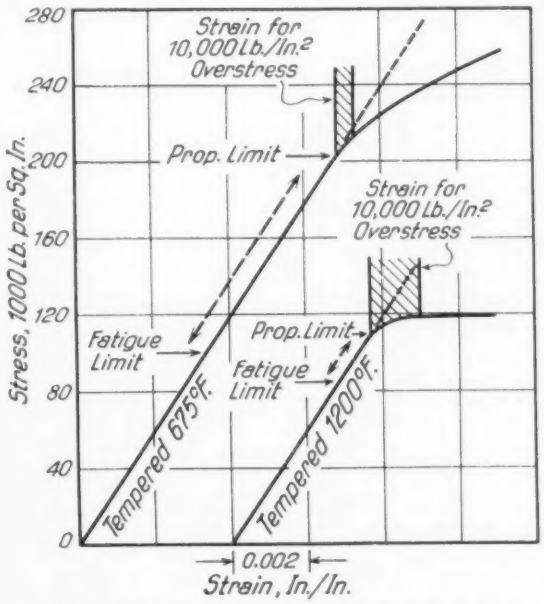


Fig. 18—Relation Between Tensional Elastic Properties and Fatigue Limits (Reversed Bending) of Nickel-Silicon Steel, 10-C Oil-Hardened from 1550 Degrees Fahr. and Tempered as Indicated.

675 degrees Fahr. At stress around the respective fatigue limits of these two crystalline aggregates there should therefore be a greater probability of individual crystals being subjected to overstrain, i. e., to stresses above the proportional limit—in the softer steel than in the harder.

But in addition to the greater probability of localized crystalline overstrain (slip) the softer samples may be strained to a greater degree by a given slight overstress than the harder ones. This becomes evident in a comparison of the stress strain curves in Fig. 18.

Localized overstrain and strengthening from the suspected particle deposition would not be expected to occur in the hard steel unless stresses appreciably above the fatigue limit were applied, since the proportional limit of the crystalline aggregate is about twice the fatigue limit.

The softer samples, with the greater probability of localized overstrain, might decay under applied stresses at or just above the fatigue limit of the crystalline aggregate. The fatigue limit actually observed with the usual testing technique of determining the life at different stresses should, then, be that of the crystalline aggregate plus the strengthening from the particle deposition in the slip planes. Improvement having already occurred no further strengthening would be expected on repeated stressing above the observed fatigue limit.

Some additional evidence is available in support of these views, apart from the known instability of many supersaturated solid solutions, and the fact that slip has been observed in many metals below the fatigue limit. As is shown in Table XIII, the decay which oc-

Table XIII
Mechanical Properties of Nickel-Silicon Steel, 10C, Quickly Cooled and Slowly Cooled After Tempering at 1200 Degrees Fahr.

Heat Treatment	Prop. Limit, lb./in.²	Yield Point, lb./in.²	Tensile Str., lb./in.²	Elong. in 2", %	Red. Area, %	Fatigue Limit, lb./in.²	Fatigue Ratio(1), %
1575° F. oil; tempered 2 hrs. at 1200° F. and							
Water Quenched	110,000	120,000	138,000	24.5	56.8	85,000	61.5
Furnace Cooled	125,000	130,000	141,250	22.0	48.6	80,000	56.5

(1) Ratio of fatigue limit to tensile strength.

curred during slow cooling of the nickel-silicon steel 10C from 1200 degrees Fahr. raised the proportional elastic limit and yield point some ten or fifteen thousand pounds per square inch above that of the undecayed steel without any significant change in the tensile strength (or hardness). While the undecayed samples had the lower elastic properties in tension tests the fatigue limit was actually a little higher than that of the thermally decayed steel, a condition which suggests

but does not establish that decay and strengthening occurred under repeated stressing.

It should also be noted that the ratio of the fatigue limit to the tensile strength of this nickel-silicon steel, oil hardened and tempered at 1200 degrees Fahr., was about 56 per cent in the samples furnace cooled from the tempering temperature and 61 per cent for those water-quenched. These values are both on the high side of the range (35 to 55 per cent) ordinarily found in steels and the latter, obtained on undecayed samples, might be a reflection of slip interference produced by particle precipitation in the slip bands formed during repeated stressing.

The data, on which these speculations are based, were all obtained on one melt of nickel-silicon steel produced in a high frequency furnace. Tests were made on a second melt, produced in an electric arc furnace with oxidizing and conditioning slags, but only samples quenched and tempered at 675 degrees Fahr. were prepared.

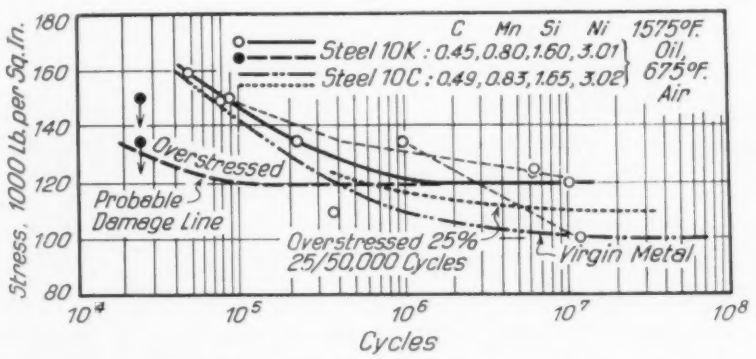


Fig. 19—Fatigue Limits and Resistance to Overstress (in Reversed Bending) of Two Melts of Nickel-Silicon Steel, Quenched and Tempered to Rockwell "C" Hardness of About 49.

It will be recalled that after such heat treatment the first melt (10C) was strengthened by overstressing but as is shown in Fig. 19 the second melt (10K) with a susceptibility to temper brittleness of 12, instead of 5, did not exhibit similar effects. It was readily damaged by overstress, although the high stress end of the stress-cycle curve for the virgin metal was about the same as that of the first melt (Fig. 19). On the other hand, the fatigue limit and the ratio of the fatigue limit to tensile strength of the second melt (10K) were higher than those of the first melt, even after strengthening by overstressing. The differences between the two nickel-silicon steel melts in the fatigue tests were, therefore, mainly in the behavior at

or close to the fatigue limit and they might result from differences in the ease of slip, the rate of decay of unstable supersaturated solid solutions, or both.

In tensile tests, the second melt of nickel-silicon steel, 10K, broke at lower stresses than the first melt, 10C, and showed a proportional elastic limit of 188,000 pounds per square inch, some 15,000 pounds per square inch lower than that of the first melt. Presumably the second melt was in a more highly stressed condition than the first and more readily susceptible to slip but the origin of the differences in behavior of the two melts in the fatigue tests is not now known. Both gave indications of solid solution decay of some sort and the dominant cause of the differences might well be in one or more of the variables cited.

At this point it may be helpful to summarize briefly the recorded observations and to differentiate between them and the hypothesis advanced in explanation of the described effects. The observations are essentially that a temper brittle nickel-silicon steel, with a susceptibility ratio of 5, showed strengthening by overstressing in repeated bending tests on oil-hardened samples and those oil-hardened and tempered at 675 degrees Fahr. Samples of the same melt oil-hardened and tempered at 1200 degrees Fahr., whether water-quenched or furnace cooled from the tempering temperature, and samples from a second temper-brittle melt, with a susceptibility ratio of 12, oil-hardened and tempered at 675 degrees Fahr. had relatively poor resistance to overstress but initially rather high fatigue limits and high ratios of fatigue limit to tensile strength. Their behavior in the usual fatigue tests, and when subjected to overstress, resembled in several aspects that of age hardened copper-silicon and nickel-aluminum steels.

It was postulated that the strengthening by overstressing in the fatigue tests and the high fatigue limits were the result of decay of supersaturated solid solutions, initiated by slip. Particle precipitation in the slip bands was conceived to obstruct slip and so to improve the resistance to fatigue.

Differences analogous to those observed in the two nickel-silicon steel melts are found in the results of tests on two normalized low carbon steels reported by Aders.[33] As is shown by the summary in Table XIV, Aders' low carbon steel (W) which showed a somewhat

[33]See footnote (7).

Table XIV

Analogy in the Behavior of Temper Brittle Nickel-Silicon Steels and Carbon Steels Susceptible to Aging Embrittlement (1)

Steel Composition, %				Steel	Susceptibility to temper brittleness	Fatigue Limit of virgin	Effect of 25% overstress for designated number of cycles on fatigue limit	
C	Mn	Si	Ni	No. (2)	or aging embrittlement	metal, lb./in.^{2}	Cycles	Effect Lb./In.^{2}
0.49	0.83	1.65	3.02	10C	5	100,000	25,000	Raised 10,000
0.45	0.80	1.60	3.01	10K	12	120,000	25,000	Damaged
0.08	0.44	0.05	....	W	Smaller than S	32,700	100,000	Increased slightly and in same amount as when strengthened by understressing
0.07	0.48	0.01	....	S	Larger than W	34,100	100,000	Damaged

(1) Data on carbon steels from tests by K. Aders, See footnote (7) of the text.
(2) The carbon steels were normalized, the nickel-silicon steels oil quenched from 1575° F. and tempered at 675° F.

smaller susceptibility to aging embrittlement than his steel S had a lower fatigue limit and was strengthened slightly by overstressing. The author's nickel-silicon steel, 10C, which showed a smaller susceptibility to temper brittleness than steel 10K, likewise had a lower fatigue limit and was strengthened by overstressing.

Aders' low carbon steel S, with an initially higher fatigue limit than steel W, was damaged by overstressing. Similarly the nickel-silicon steel 10K, with an initially higher fatigue limit than steel 10C, was damaged by overstressing.

These analogies are not submitted as proof of the hypothesis advanced in explanation of the observed effects but they suggest that the latter are perhaps more broadly prevalent and therefore of somewhat greater importance, than might be inferred solely from the results of tests on the nickel-silicon steels.

Tensional Overstrain in Temper Brittle Nickel-Silicon Steels

If slip in the fatigue tests of the nickel-silicon steel samples tempered at 1200 degrees Fahr. and water-quenched caused decay of a supersaturated solid solution and raised the fatigue limit, then the slip produced by static tensional overstress should cause decay and might perhaps be expected to become evident in stress-strain curves.

According to early researches carried out by Bauschinger[34] a tensional stress above the elastic limit, but below the yield point, should produce an immediate increase in the elastic limit, the magnitude of this effect increasing as the overstress approaches the yield point. But with an overstress above the yield point there is an immediate loss of elasticity.

If the conclusions reached by Bauschinger are generally applicable both to carbon and alloy steels in different conditions of treatment and the overstress is kept below the yield point, immediate re-testing would be expected to show an increase in the proportional elastic limit. If strengthening from the decay of a supersaturated solid solution were to be superimposed on this, a somewhat larger increase in the proportional limit might be expected than when decay was absent.

Few investigators have studied overstress within the range between the proportional elastic limit and yield point and there is therefore some doubt as to whether the conclusions drawn from the early work of Bauschinger are generally applicable.

Low carbon boiler steel, susceptible to aging embrittlement, and 2 per cent nickel boiler steels known to resist aging effects subsequent to cold work showed no increase in the elastic properties when subjected to overstress between the proportional elastic limit and the yield point even on repeated loading. When overstressed within the yield range, however, the immediate effect was a lowering of the elastic properties.

This suggests that immediate increases in the proportional elastic limit resulting from slight overstrain in the Bauschinger tests may have been due to supersaturated solid solution decay but because of the wide variations in the character and effects of aging phenomena it is not to be expected that all steels susceptible to aging will show elastic strengthening immediately after overstrain.

Absence of elastic strengthening immediately after a small overstrain is not to be taken as evidence of the absence of decay of a supersaturated solid solution since particle deposition may not always have an appreciable hardening effect; but when strengthening is observed it would seem probable that the origin is in such effects at least in steels which are initially relatively free from stress.

Tensional overstress tests were made on decayed and undecayed

[34]Mitt. Mech.-Tech. Lab. Kgl. Tech. Hochs., Heft 13, Muenchen, 1886; Dinglers polytech. Jour., Bd. 224; Civil ingenieur, 1881.

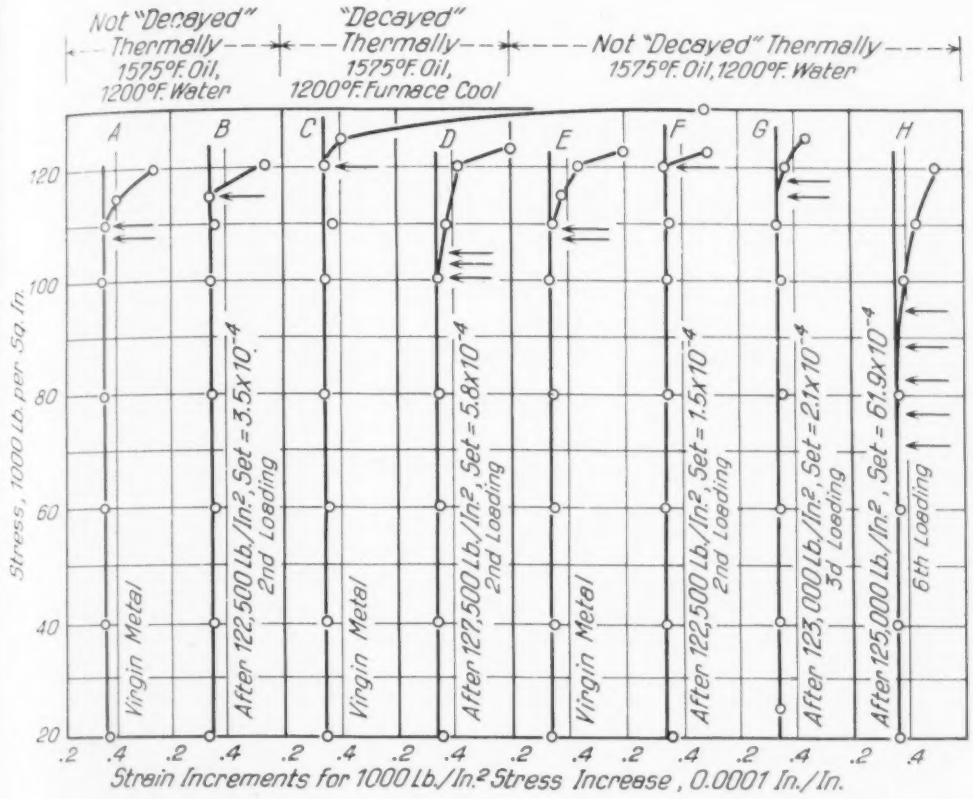


Fig. 20—Effect of Static Tensile Overstrain on the Stress-Strain Relations of Nickel-Silicon Steel (10 C) in Temper Brittle and Non Temper Brittle Conditions. Zones of Departure from the Apparent Proportionality Between Stress and Strain are Indicated by the Arrows.

samples of the nickel-silicon steel, 10C, i. e., samples furnace cooled from a tempering temperature of 1200 degrees Fahr. and samples water quenched from 1200 degrees Fahr.—and the results are assembled in Fig. 20. The tests were made with a Ewing extensometer with smallest direct reading of two ten thousandths inch and the results have been summarized, not by the usual stress-strain curves but by curves showing changes in the rate of strain with increase in stress.

Comparison of curves A and E with C, in Fig. 20, shows that the proportional limit of the steel in which decay occurred in heat treatment was higher than that of the same steel when decay was prevented before test. Small tensional overstrain, as defined by the values of set in the chart, lowered the proportional limit of the thermally decayed steel (compare C and D) but raised the proportional limit of the undecayed samples to values approaching that of the decayed steel (compare A and B, also E, F and G, with C).

These effects may be considered to support the hypothesis advanced in explanation of the behavior of the undecayed samples of the nickel-silicon steels in the fatigue tests. As the repeatedly applied stresses approached the fatigue limit of the undecayed steel,

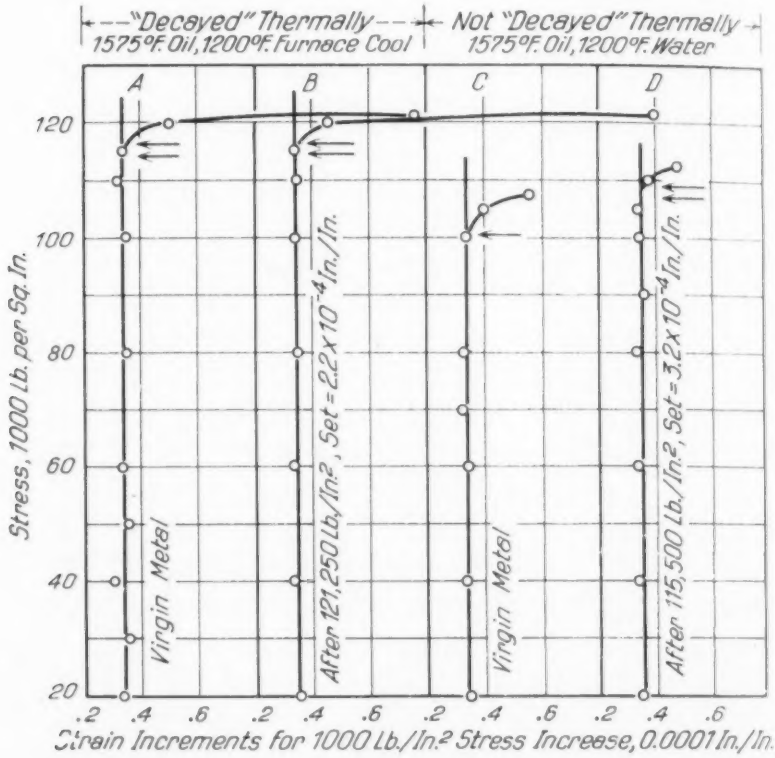


Fig. 21—Effect of Tensile Overstrain on the Stress-Strain Relations in Nickel-Silicon Steel (10 P) in Temper Brittle and Non Temper Brittle Conditions. Zones of Departure from the Apparent Proportionality Between Stress and Strain are Indicated by the Arrows. Steel Contains, 0.46 Per Cent Carbon, 0.81 Per Cent Manganese, 1.49 Per Cent Silicon, 2.94 Per Cent Nickel and 0.51 Per Cent Chromium. Charpy Impact Values When Oil-Quenched from 1575 Degrees Fahr. and Tempered 2 Hours at 1200 Degrees Fahr., were as Follows: In Temper Brittle Condition Equals 2 (Furnace-Cooled from 1200 Degrees Fahr.); In Non Temper Brittle Condition Equals 22 (Water-Quenched from 1200 Degrees Fahr.).

slip probably occurred and caused decay. Particle precipitation in the slip bands is conceived to have provided increased resistance to slip and to have raised the fatigue limit.

In carrying out these overstress tests on the nickel-silicon steel, 10C, it was intended that the set produced before reloading should be the same in the decayed and undecayed samples but there was such an abrupt departure from the apparent proportionality between stress and strain that close control of the set was difficult if not impracticable.

The set produced in the decayed steel prior to immediate reloading was greater than that in either of the undecayed samples (5.8 against 3.5 or 2.1×10^{-4} inch/inch), and in view of the Bauschinger results it may be suggested that with a smaller set there would have been an increase instead of a loss in the limit of proportionality on overstress of the thermally decayed steel (curves C and D).

Similar overstress tests were made on a third nickel-silicon steel melt, 10P, containing 0.46 per cent carbon, 0.81 per cent manganese, about 1.5 per cent silicon, 2.9 per cent nickel and also, 0.5 per cent

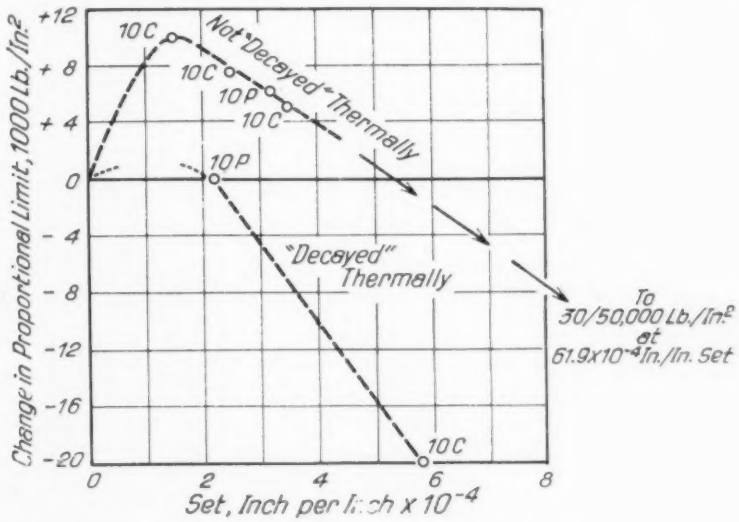


Fig. 22—Change in the Proportional Elastic Limits in Nickel-Silicon Steels, Melts 10 C and 10 P, as a Function of the Strain (Set) Produced Before Re-Testing in Tension at Room Temperatures. This Chart is to be Interpreted Only as an Indication of Differences in Behavior in the Temper Brittle and Non Temper Brittle Conditions.

chromium, and the results are shown graphically in Fig. 21. In the tests of this steel, which showed a high susceptibility to temper brittleness (ratio = 11), the overstrain applied to the thermally decayed sample (B) was somewhat smaller than that applied to the undecayed steel (D), yet the former showed no change in the limit of proportionality from overstrain while, once again, an increase was observed in the latter.

The changes in the limit of proportionality on overstrain of the thermally decayed and undecayed nickel-silicon steels 10C and 10P are plotted in Fig. 22 against the amount of overstrain (set). This combination of the results obtained on two different melts of steel, one with and one without appreciable proportions of chromium, is

intended only to show that there was a consistent difference in the behavior of the thermally decayed and undecayed steels. Only the undecayed steel appears to follow the laws deduced by Bauschinger, previously mentioned, there being no increase in proportional elastic limits observed on overstrain of the thermally decayed metals within the limits investigated.

Tensional overstress tests were also made on the nickel-silicon steel, 10C, oil-hardened and tempered at 675 degrees Fahr., one condition in which strengthening by overstressing was observed in the

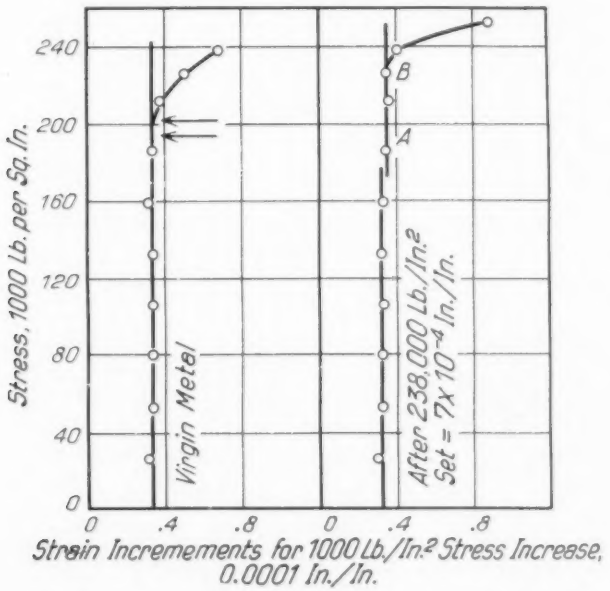


Fig. 23—Effect of Tensile Overstrain on the Stress-Strain Relations in a Nickel-Silicon Steel (10 C) Oil-Quenched from 1575 Degrees Fahr. and Tempered at 675 Degrees Fahr.

fatigue tests. Decay of the supersaturated solid solution should not have occurred with this treatment (see Fig. 14) and as is shown in Fig. 23 there is again distinct evidence of hardening from overstrain (region AB) although increase in the proportional elastic limit is not so clearly defined as in the undecayed samples tempered at 1200 degrees Fahr.

While the evidence obtained in the tension tests is all circumstantial it is consistent with the hypothesis that slip caused decay of supersaturated solid solutions in the nickel-silicon steels and, through particle deposition in the slip bands, resulted in the strengthening observed in the fatigue tests.

In the light of these results one can hardly refrain from raising the question whether the strengthening on overstressing reported by Smith[35] and by Aders[36] in tests of low carbon steels, may not also be the result of aging phenomena initiated by slip produced in their fatigue tests.

As is now well known, low carbon steels are susceptible to aging phenomena, which may be detected by impact tests on notched bars, before and after cold working followed by reheating. In some low carbon steels the losses in impact resistance, found a few moments after cold stretching, are about as large as those observed in other melts only after the cold working is followed by reheating to several hundred degrees Fahr.[37] Can it be that this rapid decay is indicative of conditions which also favor strenthening in fatigue tests?

So far, discussion of the nature of the atoms and the precipitation believed to be responsible for the strengthening effects in the fatigue tests has been avoided. Information of this sort is not readily secured since, with the usual methods of examination, the dispersion seldom has been visible in alloys susceptible to aging phenomena.

The precipitation accepted as the cause of temper brittleness may not be that which caused the strengthening under repeated stressing since the former occurs at relatively high temperatures around 1100 degrees Fahr. at which diffusion can readily take place, while the latter is observed under stresses applied at atmospheric temperatures. On the other hand the atoms now believed to diffuse most readily at atmospheric temperatures, such as carbon, are not known to produce strengthening effects comparable to those shown in the repeated stress tests. The fact that the nickel-silicon steel showed about the same fatigue limit in samples allowed to decay during thermal treatment as when decay is believed to have occurred under repeated stress suggests that the atoms responsible were of the same type in both cases. Since diffusion is an essential in aging phenomena and it does not, in general, occur as readily at atmospheric temperatures as at much higher ones, a decay caused by mechanical stresses may perhaps be viewed as an incipient atomic agglomeration whereas that which occurs during slow cooling at relatively high temperatures

[35] See footnote (6).

[36] See footnote (7).

[37] See for example, H. J. French and C. M. Schwitter, "Nickel Steels Resist Embrittlement," *Iron Age*, July 14, 1932, Fig. 2.

may be conceived to have progressed much further insofar as particle growth is concerned. But these are wholly speculations and must be left for further research.

Conclusion

In this study of the fatigue resistance of hardened steels I have attempted to assemble data which would provide an appraisal of the processes of age hardening and martensitization. But by its nature such an appraisal cannot be complete and it must be subject to changes as a better understanding is secured of the processes involved.

Hard martensites require appreciable proportions of retained austenite, or decomposition products, for high resistance to fatigue, a condition which is probably the result of the role of austenite or the decomposition products in altering the residual stresses in martensitized steels or in allowing readjustments under subsequent repeated stress.

High resistance to fatigue at high hardness may, therefore, be most readily obtained by the introduction into the steel of those elements which tend to retard the decomposition rate of austenite at low temperatures. Retained austenite appears to be much less important in medium carbon steels which are not so hard but more plastic when quenched.

The fatigue limits (in reversed bending tests) produced by age hardening of copper-silicon and nickel-aluminum steels, at around 400 Brinell, were approximately the equivalent of those obtained in martensitized and tempered steels at the same hardness. The resistance to occasional overstress of these age hardened steels was not so good, however, as that of the martensitized and tempered steels but the results obtained indicate that age hardening, which heretofore has been viewed to be more of a liability than an asset in iron alloys, can provide useful properties.

Further studies of the fatigue resistance of age hardened steels will be required before any comprehensive appraisal can be made but already it should be apparent that the processes of martensitization are no longer in the unique position which they formerly held in meeting the requirements of high hardness, high strength and resistance to fatigue in ferrous metals.

Nickel-silicon steels, susceptible to temper brittleness, showed either strengthening on overstressing in fatigue tests or initially

high fatigue ratios, up to about 60 per cent. It was suggested that these properties might be the result of aging effects, which are now known to be widely prevalent in steels, and which are believed to be due to the decay of supersaturated solid solutions. It was postulated that decay was initiated in the repeated stress tests at atmospheric temperatures, by crystalline slip. Under certain conditions this exerted a favorable influence on the mechanical properties of the steel.

While it is not certain that the precipitated particles, believed to be responsible for temper brittleness, were the same ones which caused the desirable strengthening by overstressing in the fatigue tests, circumstantial evidence suggests that the two sets of effects originated from the same source.

Further researches will be required to establish the nature of these effects and to define the conditions under which they occur, but the question may be asked whether temper brittleness, long accepted as a characteristic without virtue, may not, under certain conditions, ultimately be shown to have some assets.

In delving into some of the many interesting aspects of the hardening of steels, I have obtained a new conception of the significance of a statement made by Professor Campbell[38] many years ago. In a paper presented before the British Iron and Steel Institute in 1924 he stated: "That the atomic relations existing between solute and solvent are essentially the same in solid as in liquid solutions has become increasingly apparent during the past twenty-five or thirty years. It is now generally recognized that since steel is a solution, most of its physical properties will depend primarily on the composition and concentration of the dissolved solutes. While carbides are pre-eminently the characteristic solutes in steel, the composition of the carbides will depend not only on the total carbon, but also on the composition and concentration of such elements other than iron as may be present."

As is usual in studies relating to matters as complex as are the relations between the constitution and the properties of hardened steels, more questions have been raised than answers have been given, but I venture to express the hope that this discussion relating to a subject in which Professor Campbell was so keenly interested has been of interest to you and that it will, perhaps, stimulate further

[38] E. D. Campbell and G. W. Whitney, "The Effect of Changes in Total Carbon and in the Condition of Carbides on the Specific Resistance and on Some Magnetic Properties of Steel," *Journal*, Iron and Steel Institute, Vol. 110, 1924, 291.

researches to the end that we may ultimately gain a more complete mastery over the properties of steels.

In closing, I wish to acknowledge my indebtedness to a number of my associates for their assistance in carrying out tests, for their helpful suggestions and for their willingness to allow free use of the data described. Mr. J. W. Sands of the Development and Research Department of The International Nickel Company, Inc., has been closely associated with all of the researches from which the described data were taken. The fatigue tests and determination of retained austenite were made under the supervision of Dr. H. W. Gillett, Director, by Dr. H. W. Russell and Mr. W. A. Welcker, Jr., of the Battelle Memorial Institute. In addition, I am indebted to Dr. P. D. Merica, Assistant to the President, and Mr. A. J. Wadhams, Manager of Development and Research, of The International Nickel Company, Inc., for many helpful suggestions and the support which made it practicable to carry out such an extensive test program.

ANNUAL ADDRESS OF THE PRESIDENT

Fifteenth Annual Convention, Detroit, October 4, 1933

WILLIAM B. COLEMAN, *President*

THIS being my first opportunity to speak before a representative gathering of the membership, I assure you that it is an honor and a pleasure to present my annual report.

The operation of the Society is no different than any business organization. During the past year your Society has undergone very trying circumstances, quite similar to an approaching storm—then through the intensity of the storm and at the present moment, a gradual clearing away of the storm clouds. When your Board of Directors met in January of this year, they were faced with a business situation which had never taken place in this country before. It was necessary to carefully analyze all expenditures and operations of the Society with an endeavor to continue within our income.

The Finance Committee headed by your able treasurer, Arthur T. Clarage, met in January and prepared a conservative budget of income and expenditures for presentation to your Board. The report showed careful thought and study and was approved by all members of the Board. The Finance Committee met again in July and only minor changes were deemed necessary. The securities of the Society were carefully analyzed and certain changes in their type were recommended by the committee which were approved by the Board.

Mr. Clarage and his committee are to be highly commended for the excellent manner in which they handled our financial problems during the past year. I am sure that you members will realize the effort and thought given by the committee when you hear the treasurer's report setting forth the financial condition of the Society and its excellent outlook for this year's operation.

Shortly after the meeting of your Board, another unexpected set-back in the business world was encountered and that was the BANK HOLIDAY. As we all know, this situation caused business to reach very low proportions and it occurred at a most critical time for your Society. The annual dues for membership fell due at this crucial time. Naturally, the situation affected many individuals in their payment of dues and it was necessary for the National Office and the chapters to function as a unit in order to handle this situation. The results were most encouraging as our membership loss did not reach the proportion that seemed probable due to the Bank Holiday.

My desire during my term of office was to contact as many chapters as possible, and I felt that the greatest benefit could be obtained by meeting with the chapter executive committees. At such meetings it was possible to frankly discuss all matters pertaining to the operation of the Society as well as the local chapter. I have been able to meet with the executive committees of 90 per cent of the chapters. I trust that the few chapters I did not visit will not feel slighted as I devoted all the time I could possibly afford to such activity. I also wish to thank the executive committees of the chapters visited for their excellent attendance at these meetings and for the interest that they showed in discussing Society matters. Some of these meetings took place on evenings when the temperature was at least 100 degrees and I consider it a sacrifice for those members of the executive committees who endured such heat to spend an entire evening in the interest of your Society.

One of the phases brought up at these meetings was the question of nomination of National Officers. Considerable dissatisfaction seemed to prevail with reference to the method used at the present time. I deemed it of sufficient importance, knowing of the dissatisfaction and realizing that considerable harm could come to the Society, to bring the situation before the Board at their January meeting. After your Board reviewed the entire matter they decided to appoint a special committee of past-presidents to carefully consider the present method of nominations, and if they felt any changes were necessary, this committee was to present its recommendations to the Board. The committee, consisting of Dr. Albert E. White, Frederick G. Hughes, with Dr. Zay Jeffries as chairman, met early in April and rendered a report. This report was published in the May issue of the REVIEW and was brought up at the summer meeting of the Board for consideration. The Board recognized the merit of the report and accepted the same with the expression that changes in the Constitution should be made according to the suggestions included in this committee's report. Yesterday, this matter was thoroughly reviewed by the Constitution and By-Laws Committee together with your Board of Directors and a Cleveland attorney, in order to make sure that all phases conformed to the laws of Ohio. I wish to state that the Constitution will soon be forwarded to the membership for ratification.

Another suggestion that was brought up at almost every chapter executive committee meeting which I attended was the name of your

Society. Members individually and collectively pointed out and cited experiences where the present Society name did not convey to an executive or individual just what your Society is doing and can do for industry. We must realize that there are many persons in industry who have heard of our name but they do not have a clear conception of the broad field that is covered by the Society and merely picture the organization by whatever meaning the name AMERICAN SOCIETY FOR STEEL TREATING conveys to them. It is the executive who has the power to say where his concern will lend support either in advertising, support of chapters, or our National exposition. If the executive's interpretation was that our Society only covered a specific or a small part of the metallurgical field, then little or no support might be forthcoming, while those who know our Society and are familiar with the tremendous field covered and the great service that we have rendered industry, will support our Society in large measures. Having received so many expressions of thought at chapter executive committee meetings and knowing in my own heart that the name of the Society at the present time does not do us justice, I presented the entire situation at the summer meeting of the Board. I am happy to state that the members of the Board recognized the situation and have unanimously recommended that the name of the Society be changed so that it will be more in line as indicating our performance in the metallurgical and industrial field. I am quite sure that every one of you realizes what a difficult task confronts us when we start to change a name.

Many names were given consideration, and as a suggestion, the Board offered "American Metals Society." Since this was announced, I have written to chapter executive committee members for their further suggestions with reference to the name of the Society.

At yesterday's meeting of the Board, all replies were carefully considered and it has been decided to submit to the membership two names—AMERICAN SOCIETY FOR METALS and AMERICAN METALLURGICAL SOCIETY. This change will be presented at a later date to the membership for ratification.

I wish to assure those members who are not in close touch with the operation of the Society that there is a decided advantage to be gained by a change in the name of your Society at this time. I ask for your whole-hearted approval in this matter when it is presented to you for vote.

I wish to thank A. B. Kinzel, chairman, and Ray T. Bayless, secretary of the Publication Committee and all of its members for the work that they have done during the past year in reviewing papers and working up the splendid technical program for this convention.

My attention has been drawn to the overlapping of technical societies with reference to publications, but I have not considered the matter of serious proportion and this situation can only be rectified or kept under control by all of the societies convening and discussing a general plan.

For the past several years, L. B. Case, chairman, and J. E. Donnellan, secretary, of the Recommended Practice Committee and the committee members as well as the many sub-committees, have been going along in a very quiet and efficient manner revising practices and gathering data, to be used when the next handbook was to be published. This effort was finally crystallized in the new 1933 edition of the National Metals Handbook which will be ready for distribution immediately after this Convention. We should feel proud of the progress made by this committee, for the coming Handbook will be considerably enlarged, containing much new data and valuable information.

I wish to extend my hearty thanks to S. C. Spalding, chairman of the Constitution and By-Laws Committee, and his committee members for their splendid co-operation and work in connection with the changes in the Constitution necessitated by the change in method regarding the nomination of officers and other changes required by the Laws of Ohio.

Many members of the Society have never realized what a valuable partner they have had supporting the National Society and chapter activities. That partner is INDUSTRY.

During the past year when industry as well as our Society were encountering the stormy days, we still received the interest and support of industry in advertising for METAL PROGRESS and the HANDBOOK and the making possible of our annual convention by taking exhibit space at the exposition. Our Society through past years has always endeavored to render service to its members and to industry, and we feel that such service has been rendered, as continued industrial support to our activities would not be forthcoming if such service were lacking. This support by industry will surely be rewarded in some beneficial form to those who have helped to support

our work and we must all remember that an industrial concern is no greater than the make-up and knowledge of its personnel. I am sure that the Society has been of material benefit to each and every one of you in some form or another and thus it has placed all of us in a position to render our company better thought and service.

There are some executives who have the authority to support our activities that are not familiar with the operation of the Society. They may feel that the paying of membership dues is all that is required. It is necessary that we members of this Society enlighten those executives that are not familiar with just what the Society has done, is doing and can do, for the betterment of their personnel and their company. A great deal is due the companies that take space in our annual show. These exhibitors aid in supporting the National Metal Congress which includes the technical sessions, thus providing the material for TRANSACTIONS. Everyone of you should visit their booths when possible; give them your order for material or equipment as they are materially assisting in making possible the services rendered you each year by TRANSACTIONS, THE HANDBOOK, THE REVIEW, chapter meetings, the annual convention and many other services. Without this support you can be well assured that all of this service could not be given with the dues that you pay. Your Society would then be faced with either curtailment of service or advancement of dues. I wish to thank most heartily all companies, individuals and others who have supported the Society through advertising or taking exhibit space at the show for their faithful assistance during the past year and for its continuance.

During my visits with chapter executive committees, I have observed that all of them showed keen interest in the operation of their chapters. Naturally, the chapters have felt the effect of smaller income, but I can safely state that no chapter has suffered excessive financial losses during the year except a few who have been handicapped on account of their funds being tied up in closed banks. To such chapters the National Society has extended financial help which is just and proper. We all must realize that the chapters are the backbone of our Society and it is their activity in the past that has placed the Society in the position it holds today and their continued activity will raise it to even greater heights.

One of the outstanding accomplishments by a chapter has been the educational work performed by the Cleveland Chapter in realizing an increase in membership through this educational work, to the

extent that they have become the largest chapter in the Society. This shows excellent organization, interest and acquisition of results.

A number of chapters this year have assembled in groups for meetings and this activity should be further encouraged as it enables neighboring chapters to become better acquainted and attract larger local attendance.

Affiliated with our Society in the National Metal Congress are the Institute of Metals Division and the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers; the American Welding Society; the Machine Shop Practice Division of the American Society of Mechanical Engineers; and the Wire Association.

This assembling of societies has been of paramount importance to the success of our annual conventions. We have been leaders in this field and the splendid relationship that has grown from these assembled meetings has proven of great benefit not only to the participating societies but to their memberships as a whole. I wish to express my thanks to these societies convening with us this year and congratulate them on the fine technical programs which they are presenting this week.

I wish to express at this time, my thanks to the officers and members of the Board for the hearty co-operation they have given me. Each and every one has given willingly of his time and valuable suggestions. Very few members realize the time required by a board member away from his business in the course of a year.

It is readily understood that the Society's affairs cannot be completely carried out by the members of your Board, and we owe considerable thanks to our secretary, W. H. Eisenman, and his efficient staff for their constant, diligent and continued efforts to maintain the great service that has been rendered to individual and company year after year.

Our Society has grown by leaps and bounds since its formation. We have successfully weathered the trying times during the past two years and in order for us to continue to grow, we must have harmony throughout the entire Society so that we can all be united in increasing our membership and seeking new channels whereby we can better serve our membership and industry. Only by so doing, can we continue to thrive.

REPORT OF THE TREASURER TO THE ANNUAL MEETING—*October 4, 1933*

ARTHUR T. CLARAGE, *Treasurer*

The unaudited balance sheet of the Society as of the close of business September 30, 1933, is as follows:

ASSETS			
Cash		$ 14,834.53	
Securities (at cost)		133,987.28	
Receivables, less reserve		6,545.66	
Inventory		21,512.57	
Advances (for exposition cost, employees, chapters, post office, etc.)		7,857.02	
Office Furniture and Fixtures and Prepaid Insurance		4,516.00	
1933 Convention Deferred Expense		11,975.24	
TOTAL ASSETS			$201,228.30
LIABILITIES			
Accounts Payable (Chapter refunds)		$ 880.05	
Reserves		45,100.00	
1933 Convention Advance Receipts		23,548.75	
SURPLUS January 1, 1933	$130,698.75		
Excess Income from Operating Statement January 1 to September 26, 1933	55.69		
Appreciation on bonds	$1,009.16		
Less Surplus Charges, 1932	64.10	945.06	131,699.50
TOTAL LIABILITIES			$201,228.30

Our cash is approximately $7000.00 less than a year ago, receivables $1500.00 less, investments $1000.00 more, and inventory $3500.00 more. The market value of our securities, shown on the books at cost, has during your present treasurer's term gone down for the six months ending June 30, 1932, and risen steadily since, the market value of these securities as of July 1, 1933, being $101,617.50.

After careful consideration this year, it was decided to be to the best interest of the Society to sell certain industrial bonds and purchase additional government bonds, and a switch has, therefore, been made, which has transferred approximately $15,000.00 of industrial bonds to government holdings. An appreciation was secured on the sale of these holdings of a little more than $1000.00. The par value of all holdings is now $134,000.00, of which $49,000.00 represents government bonds. Although some of our present holdings are selling at depreciated prices, in common with all other securities, it has been deemed advisable to hold them, as a switch cannot now be made which will improve our position materially without considerable sacrifice.

It has not as yet been necessary to dispose of any securities, whatsoever, to meet operating expenses, and this year again we have been able to operate the society at a slight gain. Under the conditions that existed during the early part of this year, this is considered a most creditable showing. and has been accomplished through the paring down of Society expense.

The unaudited income and expense statement, January 1 to the close of business September 30, 1933, is as follows:

Income for the first nine months 1933	$63,892.78
Expense	63,837.09
Excess of Income over Expense	$ 55.69

The income from METAL PROGRESS advertising has continued through the year at a reduced figure, but has been met by curtailed expense. TRANSACTIONS, of course, produces no revenue, and is an expense added to the other fixed costs, including THE REVIEW, committee and board expenses, secretary and treasurer expense, and general overhead expense.

The greater portion of the expense incident to the publication by the society of the new book, "Stainless Steels," and the publication of the 1933 edition of the National Metals Handbook has already been paid and absorbed, and a considerable income expected from the sale of these publications will add to our financial position.

Although the major portion of our membership dues income has already been received, the last few months show a gain in receipts of dues of approximately 50 per cent over the corresponding months of last year, which indicates that many members are returning and new ones being added.

In connection with the remaining months of the year, it can be estimated that we may expect an excess of total income over expense for this entire calendar year of approximately $5000.00

The above, I believe, indicates that careful consideration and preparation were made for the reduced income, by the Board of Directors and management of the Society, and with METAL PROGRESS income nearly balancing expense, the society membership activities about breaking even, and the exposition at the present report showing an excess of income over expense, we believe we have now turned the much looked for corner.

I again want to voice my thanks for the co-operation of President Coleman, Mr. Eisenman and the Board of Directors, and also Mr. Ohlson, of the Cleveland office.

ANNUAL REPORT OF THE SECRETARY

October 4, 1933

W. H. EISENMAN, *Secretary*

The American Society for Steel Treating on September 30, 1933, had a total membership of 4470. Of this number 3859 or 86 per cent were of the member classification; 353 or 8 per cent were of the sustaining classification; 236 or 6 per cent were of the junior classification. The number of new applications received during the year was 524.

This is a splendid record of the members' faithfulness as well as their interest that the Society is in such a splendid condition as it is today. The credit for this is due in a large measure to the co-operation given by the chapter officers in maintaining the interest of the units of the Society.

Meetings of the Board of Directors

Since the last report to the membership, the Board of Directors has held four meetings as follows:

Cleveland—January 20 and 21
Cleveland—August 4 and 5
Detroit—October 1
Detroit—October 3

The reports of the first two meetings have been placed in THE REVIEW, and the latter two meetings will appear also in THE REVIEW.

Group Meetings

The Southern Ohio chapters held a sectional meeting in Cincinnati the latter part of March. This was a one-day meeting, with sessions morning, afternoon, and a dinner meeting in the evening.

The Columbus, Cincinnati, and Dayton chapters co-operated in making this meeting a success, and there was representation from approximately 12 chapters.

Educational Activities

Many chapters are planning educational courses for the present season. According to the information now available at the National Office:

Cincinnati is sponsoring a course on the metallurgy of iron and

steel at the University of Cincinnati. Dr. G. M. Enos is presenting the series of lectures, which begins September 25.

Cleveland is holding two courses at Case School of Applied Science. The first will be devoted to the problem of welding engineering and metallurgy. This will be given by Robert E. Kinkead. Following this, Harry B. Pulsifer will conduct a series of lectures on metallography.

Detroit, through its educational committee, has prepared a three-year course in metals which will start on October 23 at the Detroit City College, under the direction of E. B. Drake. The first year will cover foundry practice, the second year will cover the manufacture of steels, and the third year, the heat treatment and metallography of steels.

Golden Gate Chapter has already started its lecture course at Humboldt Evening High School under Howard S. Taylor. This chapter is also sponsoring both beginners' and advanced laboratory courses for men who have previously attended the lecture course. Mr. Taylor and George A. Nelson are instructors for the laboratory classes.

Communications have been received from Hartford, indicating that they also plan to carry on educational activities during the coming season.

Philadelphia chapter is co-operating with Temple University in presenting a course on heat treatment and metallography of steel. Horace C. Knerr is director of the course. It is also contemplated to start a lecture course in January under the management of the chapter.

Howe Medal

The tenth award of the Henry Marion Howe Medal, established in 1923 in honor of the first honorary member of the A.S.S.T., Professor Henry Marion Howe, was awarded at the annual banquet in 1932, held in Buffalo, to Dr. Francis M. Walters, Jr., Cyril Wells, Maxwell Gensamer and John F. Eckel, for their paper, "Alloys of Iron, Manganese and Carbon," which was considered by the award committee as the most outstanding contribution to the science published in TRANSACTIONS during the preceding year.

Campbell Lecture

This lecture, established in 1925 by the Board of Directors, and

honoring the memory of Professor Edward DeMille Campbell of the University of Michigan, was presented in 1932 at the convention in Buffalo by Edgar Collins Bain, research metallurgist, U. S. Steel Corporation at Kearny, N. J. The lecture was entitled, "Factors Affecting the Inherent Hardenability of Steel."

President's Medal

The President's Medal was presented to Past President J. Mitchell Watson at the Buffalo convention in 1932. The presentation of this medal was a tangible notification to Mr. Watson of the sincere appreciation of the Society for his splendid and valuable work as president of the A.S.S.T.

Recommended Practice Committee

Because of the preparation of the 1933 Edition of Metals Handbook, the last twelve months have been the most active the Recommended Practice Committee has had. Practically the entire program of the Committee has been devoted to the production of the new HANDBOOK.

Revision of Handbook

To prepare the new Handbook, the Recommended Practice Committee called into active duty all the sub-committees that had prepared reports or practices at any previous time for the Handbook, requesting them to revise their work and bring it up to date. All authors were requested to follow the same procedure. As a result the Recommended Practice Committee had 48 sub-committees with an approximate membership of 300 working on the reports and practices, and 120 individual authors. This program was mainly conducted by the Recommended Practice Committee by mail and required about eight months of intensive committee work.

Technical Committees—The Sub-Committees that were temporarily called into duty for the purpose of revising the book become inactive again now that the work is completed. However, the Recommended Practice Committee has nine sub-committees which are to remain active for the purpose of completing their present assignments or to undertake new problems. These sub-committees are as follows: Sub-Committee on Forging Steels, on Gas Carburizing, on Hardness Testing of Metals, on Heat Treating (General), on Heat Resisting Alloys, on Machinability of Steel, on Heat Treatment of Tool Steels, on Pickling of Steel, on Physical Constants of Metals.

The following sub-committees completed new reports or practices during the last year and have been temporarily discharged from active duty: Sub-Committee on Melting of Steel, on Nitriding, on Plastic Deformation in Pure Iron, on Quenching Equipment, on Quenching Media, on Heat Treatment of Carbon Steel Gears, on Testing and Inspecting of Bolts, Screws and Nuts.

Joint Committee on Heat Treatment Definitions—The report on Heat Treatment Definitions prepared by representatives from the A.S.T.M., S.A.E., and A.S.S.T. has been adopted by the three participating Societies. The Joint Committee was therefore, discharged from active duty February of this year. It is interesting to note that this is the first time in ten years that this Joint Committee has been inactive.

Classification of Articles—The Recommended Practice Committee has adopted a new scheme for the arrangement and compilation of the articles and practices. Under this plan each article bears a symbol and a number indicating the alloy and group to which it belongs. Thus the articles will all be compiled with a definite plan and outline in mind and can, as completed, be located in their proper sequence and section of the HANDBOOK.

Contents of New Handbook—The 1933 Edition of Metals Handbook contains a few pages over 1500. Approximately 1000 pages are devoted to the ferrous section and 500 pages to the nonferrous section.

There is a total of 228 articles for both the ferrous and nonferrous sections of the HANDBOOK, compared to a total of 148 articles in the 1930 edition.

Revisions—The ferrous section of the old HANDBOOK contained 95 articles. Seventy-six of these articles were revised or completely rewritten by the authors or sub-committees. The articles in this section that were not revised consisted mainly of tabular data of a standard nature.

The nonferrous section of the old HANDBOOK contained 53 articles of which 38 were revised and brought up to date by the authors and committees. The articles in this section that were not revised were reviewed by the authors and committees, but considered accurate for republication.

Exchange of Handbook—The plan of exchanging the old HANDBOOK for the new edition is again to be followed. A notice has been published in the REVIEW, TRANSACTIONS, and in a general letter sent

to the members instructing them that the new book will be ready for distribution and exchange on October 10th.

Nonferrous Committee—The Nonferrous Data Sheet Committee of the Institute of Metals Division of the A.I.M.E. has been very active in the co-operative arrangements with the Recommended Practice Committee. Because of the splendid work of this Committee, many new and valuable articles have been incorporated in the nonferrous section of the HANDBOOK.

The Board of Directors has followed the work of this committee, under the able direction of L. B. Case as chairman, with great care and admiration and votes it a laurel for its outstanding accomplishment.

Mr. Donnellan, secretary of the Recommended Practice Committee, has proven himself a splendid organizer and the 1933 edition is a monument to his ability.

Report of Metal Progress

METAL PROGRESS during 1933 has carried on, constantly matching the standard of excellence set at its foundation three years ago. Curtailed income from advertising has forced a regrettable reduction in size of the monthly issues. Nevertheless, a well-balanced editorial section has been maintained, containing nothing but exclusive articles, well written and illustrated, about current improvements in metals and their treatment.

Perhaps the best gage of the so-called "reader interest" in METAL PROGRESS is the requests received at the National Office for trade literature offered by its advertisers. Such material has been listed rather inconspicuously in every issue for three years, yet no less than 8274 requests for new bulletins were received during the months of January to August, this year inclusive—over one thousand a month! Here again METAL PROGRESS is making history—cautious publishers have based extensive promotional campaigns on far less generous response from their readers.

Retrenchment in every department has kept the expenditures in line with income. With the improvement in business already evident, the size and diversity of the magazine can be extended with little extra cost other than paper and postage. Meanwhile I recommend for your most cordial appreciation those stout-hearted businessmen who maintained their contact with you, the best audience in the metal industry, through the pages of METAL PROGRESS.

Stainless Book

In addition to his work on METAL PROGRESS, Editor Thum has organized and carried through to publication an encyclopaedic work on heat resisting and corrosion resisting alloys of chromium. Under the title "The Book of Stainless Steels," he has enlisted the co-operation of 75 acknowledged experts in various phases of production, fabrication, and consumption (most of them are members of A.S.S.T.) and produced a 600-page volume which is right up to the minute and representative of the best American practice. There is a distinct need for such a volume, as the only systematic book now available was written by an English metallurgist and represents English conditions. Our new book is prepared especially to answer questions raised by consumers and fabricators and hence will appeal to a wide audience. We have already received many pre-publication orders. Deliveries will be made during the present month.

Publication Committee

The Publication Committee for the year 1933 is made up of the following: A. B. Kinzel, Chairman, Ray T. Bayless, Secretary, G. R. Brophy, E. H. Dix, Jr., Alex. L. Field, Arthur E. Focke, M. H. Frommann, T. L. Joseph, R. L. Kenyon, T. Holland Nelson, H. S. Rawdon, C. B. Sadtler, Robert Sergeson, W. P. Sykes, H. S. Taylor.

Throughout the year and up to the present date the Committee has reviewed 55 papers, of which 43 have been approved.

No meetings of the Publication Committee were held during the period from October 1932 to October 1933. However, the chairman and secretary have held several conferences in regard to the activities of the Committee. Otherwise, the activities of the committee have been transacted by mail. A meeting of the Committee was held at 4:30 P. M. on Monday, October 2, 1933.

Transactions

There has been published since the last annual meeting the last three issues of Volume 20 of TRANSACTIONS (October, November and December, 1932) and nine issues of Volume 21, (January, February, March, April, May, June, July, August and September, 1933). The three issues of Volume 20 contained 300 pages, each issue of TRANSACTIONS containing 100 pages and the first nine issues of Volume 21 contained 900 pages. It has been decided due to the fact that

each issue of TRANSACTIONS carries 100 pages, that it would be preferable to have a volume cover the period of one year thus making a 1200 page volume for the year. Volume 21 will, therefore, contain the 12 monthly installments of TRANSACTIONS for the year 1933.

TRANSACTIONS as published since September 1932 contains papers presented during the 1932 Convention, together with others received during the year. 13 papers were published in the October, November and December issues of Volume 20 and 38 papers in the January, February, March, April, May, June, July, August and September issues of Volume 21.

An analysis of the editorial production of TRANSACTIONS from Volume I through the September 1933 issue of Volume 21 shows a grand total of 19,907 pages.

Preprints

At the Buffalo Convention last year there were 28 papers presented on the technical program, 12 of which had been prepared and distributed to members. The total number of pages of preprints for that year was 236.

This year 21 papers have been prepared in preprint form out of a total of 30 papers scheduled on the technical program, with a total number of 452 pages. These were made available to the members of the Society on August 31 and were sent to all members having requested them.

The number of requests for preprints this year has been equally as large as that for the past two years, indicating that the interest of the members in the preparation of written discussion is still active.

Review

During the past year THE REVIEW was changed from a monthly newspaper to a bi-monthly. Since the first of the year it has appeared every other month beginning with January. To take care of the additional material which would appear in a bi-monthly, the average size of THE REVIEW was increased from four to six pages.

The September issue, which had a circulation of 20,000 among the members of all societies and divisions co-operating in the 1933 National Metal Congress, was eight pages.

From October, 1932, to date (7 issues) 2308 column inches were devoted to editorial matter and 732 to advertising. The amount of REVIEW space devoted to reports of chapter meetings was 1098

column inches, or somewhat more than one-third of the entire space during the year.

President's Bell

The President's Bell, which is awarded to the chapter whose activities have been of outstanding merit for the preceding year, rested last year in the custody of the Montreal chapter, having been awarded to that chapter by President d'Arcambal.

The award of the President's Bell rests exclusively upon the decision of the president of the Society.

You will have observed from the auditor's report published in the May issue of THE REVIEW that the total receipt of dues for 1932 were $55,874.13. Of this amount, $23,454.36, or 43 per cent was returned to the chapters.

The total assets of the chapters at the close of the fiscal year of June 1933 were $41,600, an increase of $3000.00 over the assets of the preceding year. This is a splendid showing, when general conditions are taken into consideration.

As stated in the last annual report, the financial income of the Society could not help but reflect the current business conditions, and last year for the first time in the fourteen years the Society has been in existence, there was a deficit.

It may be interesting to note that by practicing the most severe economies, exercising greater energy and progressiveness, the Society has every prospect this year of returning to its previous record of having an excess of income over expenditures.

It may be further interesting to know that the sale of advertising in the National Metals Handbook is larger this year than in either of the two previous editions, 1929 and 1930, the total amount being $5265.00.

This represents a 60 per cent increase over the original estimate for the sale of advertising in this year's edition of the HANDBOOK.

Response has been splendid for advertising in the OFFICIAL PROGRAM, and that has exceeded by 70 per cent the contemplated receipts.

The Exposition now in progress reflects the current change of conditions and has 30 per cent more exhibitors than last year, as well as exceeding by 40 per cent the space sales of last year's exposition.

The receipts from dues for July, August and September 1933 have been double the amount received in payment of dues in the corresponding months of 1932.

While it is true there has been a decrease in the number of new applications received, it is felt that with the many educational courses being presented by the chapters, in which membership in the Society is necessary before an individual may enroll in the course, there will be a considerable increase in the membership of the Society over the next few months.

REPORT OF 1933 NOMINATING COMMITTEE

The annual meeting of the Nominating Committee of the American Society for Steel Treating, was called to order by W. H. Eisenman October 2, at 10:00 A. M. The credentials of the several delegates were examined and found in order. Thirty chapters were represented with Lehigh Valley, St. Louis and Springfield absent.

J. Fletcher Harper was selected as chairman of the meeting and Wayne L. Cockrell as Secretary. The chairman appointed Messrs. Howard J. Stagg, John J. Crowe and Walter G. Hildorf as the notification committee.

Nominations for President were entertained by the chair. N. I. Stotz of Pittsburgh nominated W. H. Phillips. W. G. Hildorf of Canton-Massillon seconded the nomination of Mr. Phillips. J. J. Crowe of New York moved nominations be closed—seconded by Robert Atkinson of Detroit. The motion carried. Vote on nomination was favorable.

Robert Atkinson moved unanimous selection of Mr. Phillips. Motion seconded and carried.

Nomination for Vice-President, H. J. Stagg of Syracuse nominated B. F. Shepherd of Lehigh Valley Chapter. S. C. Spalding of New Haven seconded. J. A. Comstock, Chicago, nominated Dr. Paul D. Merica. E. W. Esslinger of Cincinnati seconded.

Robert Atkinson moved nominations be closed. Seconded and carried. First ballot showed B. F. Shepherd twenty, Merica ten. Moved and seconded that Mr. Shepherd's nomination be made unanimous. Motion carried.

Nomination for Treasurer. A. T. Clarage of Chicago, was nominated by J. R. Adams of Philadelphia and seconded by L. L. Wyman of Schenectady. W. G. Hildorf moved nominations be closed, N. I. Stotz seconded. Motion carried. A. T. Clarage nominated by acclamation.

Nominations for two National Directors. E. L. Bartholomew

of Boston nominated Dr. George B. Waterhouse. Seconded by B. A. Bovee of Buffalo. Robert Atkinson, Detroit, nominated William P. Woodside, seconded by W. G. Hildorf.

J. J. Crowe of New York, nominated E. C. Bain and L. L. Wyman seconded. W. L. Cockrell of Tri-City, nominated George A. Uhlmeyer, seconded by C. B. Sadtler of Rockford. H. J. Stagg moved nominations be closed. Seconded and carried.

N. I. Stotz moved 16 votes be required to nominate and any candidate securing that number be declared elected and if a second ballot was required, the low on the first ballot be dropped. J. J. Crowe seconded. Motion carried.

First Ballot.

E. C. Bain	24
W. P. Woodside	19
G. B. Waterhouse	14
G. A. Uhlmeyer	3

J. J. Crowe moved nominations of E. C. Bain and W. P. Woodside be made unanimous. Seconded and carried.

The nomination of the committee thus secured, were:

W. H. Phillips for President
B. F. Shepherd for Vice-President
A. T. Clarage for Treasurer
E. C. Bain, W. P. Woodside } For National Directors.

The meeting adjourned after a few speeches expressing complete satisfaction with results of the committee's work.

Editor's Note: Section 4a of Article XI of the Constitution of the Society requires that "it shall be the duty of the nominating committee to secure and file with its nominations the written consent to serve of each person named by the committee." J. Fletcher Harper in reporting the results of the nominating committee meeting to the annual meeting of the society Wednesday October 4, 1933, said

"The nomination for the treasurership was tendered to the present incumbent, Arthur T. Clarage, who was compelled to refuse such nomination, and the sub-committee, therefore, nominated Emil Gathmann of Baltimore who accepted the nomination."

THE MECHANISM OF CRYSTAL GROWTH

By Wheeler P. Davey

Abstract

The author takes up in systematic order the experimental evidence as to the growth of crystals from the vapor, from the melt, and from the solid, and discusses the physical conditions which are associated with each. It is shown that in every case imperfection is the natural state of a crystal. Following the general lines of the theory of Zwicky, the author builds up a detailed theoretical picture of the growth of crystals. This picture is such that imperfections are seen to be inherent in the structure. The ordinary properties of materials (such as manner of crystal growth, tensile properties, segregation of impurities, properties of the melt, etch figures, and segregate structures of the Widmanstatten type) all follow as natural corollaries to this picture.

THE importance of the mosaic structure of crystals is a matter of common knowledge to all crystal analysts. Perfection in single crystals is so rare that we may confidently assume imperfection to be their normal state. It will be of interest, therefore, to examine the various ways in which crystals may be grown in the hope of finding mechanisms of crystal growth which will lead easily to the mosaic type rather than to the perfect type of structure. If any such mechanism is to have real value it must necessitate the existence of demonstrable crystal properties which are distinct from the data which lead to the mechanism. The present paper deals, therefore, not only with the evidence leading up to a picture of the mechanism of crystal growth, but also with the consequences of that mechanism in determining certain of the properties of crystals.

The Growth of Crystals

There are, in general, four ways of growing crystals: (1) from the vapor, (2) from the melt, (3) from solution, and (4) from less

A paper presented before the Fifteenth Annual Convention of the society, Detroit, October 2 to 6, 1933. The author, Wheeler P. Davey, is research professor of physics and chemistry, School of Chemistry and Physics, Pennsylvania State College, State College, Pa. Manuscript received March 18, 1933.

stable crystals in contact with the growing crystal in a continuous solid. We will take up each of these in turn.

(1) Growth from the Vapor—If the vapor of a substance is allowed to come in contact with a cold surface it will condense to form a solid. X-ray evidence in the case of nickel(1)* shows that if the surface is at a sufficiently low temperature, this solid material is amorphous. If the surface is at a high enough temperature the solid material is crystalline. It is only rarely in actual practice that vapors are condensed at low enough temperatures to give truly amorphous solid condensates. For each substance we may imagine a critical temperature below which it is almost impossible to obtain a crystalline deposit. The higher the temperature above this limit, the more readily will the deposit crystallize. In the case of nickel the amorphous condensate may be obtained on a surface cooled with water. If the surface is heated to 400 degrees Cent. (750 degrees Fahr.) a deposit is readily obtained, which is composed of small crystals. An amorphous layer 10^{-5} centimeters thick apparently is sufficiently insulating so that the latent heat from further condensation of nickel raises the surface temperature enough to yield crystals.

These facts can be explained if we make three simple assumptions. (a) Atoms of nickel which hit a sufficiently cool surface do not bounce off elastically, but remain on that surface. In other words, every atom which hits the surface "condenses". If it evaporates subsequently it must have gained from neighboring atoms enough kinetic energy to overcome the energy of its cohesion to its neighbors. This assumption is identical with that made by Langmuir(2) to explain certain of his data on evaporation and condensation. (b) If the temperature of the condensing surface is low enough, every atom which hits the surface must stay practically in the place where it hits. If the temperature of the condensing surface is high enough, it is assumed that each condensed atom can migrate on the surface like a molecule of a two-dimensional gas until it happens to find some spot where it can help to build up a crystal. In such a spot the potential energy of the atom would be at a minimum and its chance of further migration would be vanishingly small. This assumption is apparently necessary in order to make it possible to grow crystals of nickel in the neighborhood of 400 degrees

*The figures appearing in parentheses pertain to the references appended to this paper.

Cent. (750 degrees Fahr.). Such temperatures are much too low to permit the evaporation of any appreciable number of atoms from the surface,[1] so that evaporation alone cannot rid the surface of improperly situated atoms whose locations do not fit the positions demanded by the crystal structure of nickel. (c) When a crystalline surface has once been formed, newly condensed atoms have only to move two or three atomic diameters to find appropriate stations in the structure. If the condensing atoms could be made to impinge uniformly on the crystalline surface we might expect to grow very perfect crystals. It is, however, inherent in the kinetic theory of gases that the atoms must hit the surface in irregular groups much like the pitter-patter of rain on a roof. Although, on the average, as many atoms will hit on one portion of the surface as on any other portion, we must assume that the distribution from instant to instant will be very nonuniform. This leads inevitably to minute imperfections in the crystals so that what appears at first to be a single crystal is really a mosaic of tiny crystals having almost exactly the same orientation. If we grant this picture, we would expect to grow reasonably perfect crystals from pure vapor only at exceedingly slow rates of condensation at temperatures close enough to the melting point to permit all imperfections to be wiped out by the migration of atoms within the crystal. Such conditions are not usually found in practice. Even if ideal thermal conditions were realized, minute traces of impurities in the vapor will tend to deposit in patches here and there on the surface in layers one molecule (or atom or ion) thick. These layers of impurity will tend to foul the surfaces of the patches, thus limiting the growth of the crystal to small separate portions of the surface.[2] It would seem, therefore, that in general when a crystal is grown from vapor an approximation to the "ideally imperfect" state is really the normal state of the crystal.

Under exceptional circumstances, not easily controlled in the laboratory, the tendency for some parts of the surface to grow faster than other parts becomes especially great. Macroscopic needles or even fin-like projections are sent out in advance of the growing surface giving the dendritic type of formation so well known to metal-

[1] According to the International Critical Tables, Vol. III, p. 205, nickel has a vapor pressure of only 10^{-3} centimeters of mercury at 1250 degrees Cent. (2260 degrees Fahr.). At 400 degrees Cent. (570 degrees Fahr.) it should have a vapor pressure of the order of 10^{-16} centimeters of mercury.

[2] A possible mechanism which is capable of explaining this effect in detail will be described later in this paper.

lurgists. They appear to show on a large scale the consequences of the same sort of "group growth" on a crystal face which the kinetic theory of gases forced us to assume on a submicroscopic scale. Apparently, imperfection is the normal state of a crystal grown from the vapor. We shall soon see that imperfection is the normal state of all crystals no matter by what process they have been grown.

(2) Growth from the Melt—Growth of crystals from the melt does not take place simultaneously in all parts of the liquid. Either a seed crystal is present and growth proceeds out from this seed, or spontaneous nuclei of crystallization are formed, each of which acts as a seed.

(a) We may feel safe in assuming that the molecules[3] in the melt wander about with almost random motion. This implies that there is a chance of several molecules colliding together in just the configuration to form the beginning of a unit-crystal. In the simplest case, if the temperature is high enough, these molecules will have enough thermal energy to part company in spite of the crystal forces holding them together[4]; i.e., above the melting point the chance of disaggregation exceeds the chance of aggregation. We are tempted at first to assume that below the melting point the chance of aggregation exceeds the chance of disaggregation and that at the melting point the two chances are equal.(3) Closer study of the forces, acting between molecules, shows that this simple picture must be modified somewhat. These modifications are of such a nature as to make it possible not only to account for a sharp freezing point in the presence of a trace of the solid, but also to account for the possibility of undercooling in the absence of the solid.

If a seed crystal is placed in a perfectly insulated[5] melt at its freezing point, the crystal will neither melt nor grow. If, however, the heat insulation is not quite perfect, the environment of the melt will act as a slight heat-sink and the seed crystal will grow without

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[3]In this discussion the word molecules will be used as a convenient general term to include molecules, ions, and atoms.

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[4]In growing a crystal from the vapor a molecule which collides with the crystal surface is held by the forces of cohesion which are characteristic of the crystal. In growing a crystal from the melt the apparent forces tending to hold the molecules on the surface are equal to the difference between the real forces of cohesion and the forces between these molecules and the surrounding liquid. This difference in the sizes of the resultant forces accounts for some of the differences in the pictures of the mechanisms of crystal growth in the two cases.

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[5]The effect of perfect insulation may be obtained by keeping the material around the melt at the same temperature as the melt itself so that the melt neither gains nor loses heat. It is assumed that the melt is somewhat above the room temperature.

any measurable change in the temperature of the melt. This is because molecules which are systematically oriented and marshalled in a crystal are held together by forces which are more or less chemical in their nature. The potential energy of such a system is therefore less than that of a chaotic arrangement such as the melt would have. The energy thus liberated is the latent heat of crystallization, and is numerically equal to the latent heat of fusion. It is this energy which must be absorbed by the heat-sink. If C represents the cohesive force of the macroscopic seed crystal, L the forces between the liquid and the surface of the crystal, and D the forces tending to disintegrate the crystal due to thermal agitation, then the temperature at which the seed crystal can grow is an infinitesimal amount lower than the temperature for which

$$(C - L) = D \qquad (1)$$

For a given material, then, the temperature at which a seed crystal can grow is definitely fixed. This temperature is defined as the freezing point of the melt.[6]

The difficulty of starting spontaneous crystallization may be explained as follows. Let us consider at first a melt made up of the simplest kind of molecules, for instance a metal whose molecules are monatomic. In order to form a spontaneous nucleus, several molecules in the melt must collide in the configuration which is characteristic of the crystal of that substance. In the melt such nuclei are probably made and broken up continually. In the case of an embryo nucleus made up of only three or four molecules, a given molecule is not held to the group by as many immediate neighbors as would have held it if it had been a part of a "flat" surface of a massive crystal. This means that the cohesive forces of the newly formed spontaneous nucleus cannot be quite as large as the quantity C of equation (1). If we define the melting point in terms of equation (1) it follows from this picture that, at the melting point, the

[6] Many cases of so-called spontaneous crystallization without undercooling are really started by extremely fine seed crystals which enter the melt from the air. The difficulty encountered in crystallizing anhydrous glycerine (freezing point 17.9 degrees Cent) is proverbial; yet the story is told of a laboratory in a cool climate which, having once produced crystals of glycerine, had difficulty in keeping any of its stock fluid. Tutton relates (4) a story told at a meeting of the Royal Society, of how a newly synthesized compound could not be crystallized for several days under what should have been optimum conditions. After the compound had been manufactured for some time, the air of the laboratory became contaminated with spontaneous nuclei formed from the dust of the dried material and scattered by the daily handling of the material in the laboratory. After these nuclei were formed there was no further difficulty in crystallizing the material. Apparently we must assume that "crystal germs of most common crystallized substances, of no larger size than bacteria, are floating about in our atmosphere, ready at any time to drop into our solutions and, if the latter are in the proper receptive condition, to set them crystallizing."

average tendency for disaggregation of spontaneous nuclei exceeds the average tendency for aggregation so that a spontaneous nucleus has no chance of persisting long enough to grow. In order that growth of the spontaneous nucleus may begin, it is necessary to undercool the melt below its freezing point. In other words, we must lower the temperature (and therefore the value of D of equation (1)), until the nucleus can persist long enough for some other molecule to collide with it at some point so close to the correct spot that the molecule can migrate easily to its proper location. According to this picture a thoroughly melted liquid cannot crystallize spontaneously unless it is cooled below its freezing point. The amount of undercooling necessary should be a property of the substance to be crystallized.

The case of less symmetrical molecules, such as those of organic substances, is complicated by the additional consideration that, in order to form a spontaneous nucleus, several molecules must not only collide to form the correct configuration of molecules, but their orientations must be such as to give also the correct configuration of atoms. Such a restriction greatly decreases the chance of forming spontaneous nuclei, and therefore tends to decrease the concentration of nuclei in the melt. This effect may be partly compensated by the longer life of the nuclei, caused by the increase in resistance to disaggregation resulting from the large number of atoms which serve as points of attachment between molecules in a nucleus. At first sight it would seem that the net effect of these two opposing tendencies should largely determine the amount of undercooling possible for a given substance. It is conceivable, however, that not only in complicated substances, but even in simple substances like metals, the resistance to disaggregation may be so strong as to bring in still another effect. When a material is melted without raising the temperature perceptibly above the melting point, small crystal fragments the size of spontaneous nuclei may slough off from the crystal and float around in the melt for long periods.[7] The effect

[7]This hypothesis is consistent with the experimental results of A. Goetz (5). He found that the orientation of single crystals of bismuth, grown from a single seed in the melt, depends upon orientation of the portion of the seed which has just melted, rather than upon the orientation of the unmelted portion. This effect disappears when the bismuth is heated 10 degrees Cent. above its "melting point." It is as though the "melted" portion of the seed contained sloughed-off crystal fragments from the mosaic. A. Mueller (*Proc. Roy. Soc.* 127, 417, (1930) directed a fine beam of X-rays on some molten paraffin very near a crystal of the same substance. For a small range of temperature above the melting point the diffraction pattern showed that there was still a considerable amount of orientation among the molecules. Apparently the crystal dissolves in "sheets" of molecules. It is interesting to note, too, that Traube and von Behren have found (6) that, when a crystal is dissolved into an almost saturated solution, ultramicroscopic particles can be found which persist for some time before being dissolved to a true molecular dispersion.

should be that of greatly increasing the concentration of nuclei and thus of promoting crystallization of the melt at the freezing point when the proper heat-sink is brought into play. This increase in concentration of effective nuclei should increase the chance of a molecule from the melt colliding with a nucleus at the proper place and with the proper orientation. In other words, it should be difficult to undercool a material which has been melted without raising the temperature appreciably above the melting point. If, however, the liquid is strongly heated to bring it considerably above the melting point, the sloughed-off crystal fragments should all disintegrate, thus bringing down the concentration of effective nuclei to the normal value for that material. In view of the difficulties in crystallization caused by the necessity for molecular orientation, the reduction in the concentration of nuclei by heating should greatly increase the possibility of undercooling.[8]

It is evident from this discussion that, except for mechanical inclusions, impurities can be included in the body of the crystal only if the size and shape of the molecules of the impurity are such as to permit them to fit easily into the structure of the crystal and if, besides, the chemical forces between the crystal and the impurity are at least equal to C of equation (1). It will be sufficient for our present purposes merely to point out that the ordinary practice of purification of materials by slow crystallization of a part of the melt is consistent with the picture of crystallization which we have presented here. It is a consequence of the picture that, if a melt is cooled slowly enough from one end, the impurities tend to concentrate in the last portion to crystallize. If crystallization proceeds too rapidly, so that crystal nuclei appear throughout the whole body of the liquid, then the impurities must concentrate at the grain boundaries. If crystallization is still more rapid, some of the impurities must concentrate at the boundaries of the mosaic of which each macroscopic crystal is composed. These predictions from the theory are consistent with the results of metallurgical practice.

(b) Now that we have seen, both in the case of a seed crys-

[8]This picture is really a detailed expansion of that given by Othmer(3) and Tammann(7). Another picture given by Richards(8) differs from this primarily, (a) in substituting a foreign adsorbent for the crystal fragments sloughed off from the melting solid, and (b) in substituting a portion of the melt adsorbed on the foreign adsorbent for the oriented molecules which we have pictured as colliding with the crystal fragments or with true spontaneous nuclei. In both these pictures the forces called into play by orientation take the whole matter out of the field of thermodynamics.

tal and in the case of a spontaneous nucleus, how crystallization starts, we must take up the manner in which the seed or the nucleus grows to form a finished crystal from the melt. The following experiment(9) will serve as an illustration of the process. A test tube is filled with lump photographic hypo ($Na_2S_2O_3 \cdot 5H_2O$) and is heated over a bunsen burner to melt the hypo. With a little practice this can be done without losing much of the water of crystallization. At first the molten hypo will appear cloudy but in a few seconds a clear transparent liquid is obtained. A large watch glass is warmed by dipping it into boiling water and is then quickly mounted so that it can be illuminated properly from below. The molten hypo is poured into the watch glass and a single crystal of hypo is immersed in the melt at the center of the watch glass. It is best to handle this single crystal with warm, chemically clean, dry tweezers. Very soon small needles will be seen projecting out from the surface of the crystal. Under favorable conditions of illumination it may be seen that these needles lie in three directions which are definitely oriented to the axes of the crystal. They tend to form a three-dimensional meshwork with liquid hypo in the interstices. If the volume of material, rate of cooling, and conditions of illumination are all favorable, these needles may be seen to grow still other needles on their sides so that the original meshwork becomes the frame for a very much finer meshwork.

It is easy to imagine(9) this process repeating itself to give a whole succession of such meshes each finer than that from which it is hung, so that we are tempted to assume the existence of an ultimate three-dimensional meshwork of such fineness that it could not even be seen with a microscope. Eventually the whole mass of liquid becomes crystallized, and if the conditions of the experiment may have been favorable a large "single" crystal of hypo is obtained. When we remember the marked changes in volume which most materials undergo on solidification, we are led to assume that the last traces of liquid to crystallize out must yield solid material which is under considerable strain. These strains may even be thought of as distorting the fine meshwork so as to change slightly the orientation of the tiny crystal fragment which this meshwork encloses. This distortion will, of course, be increased by the sharp temperature gradients due to the local liberation of the latent heat of solidification. Such a picture leads us at once to the conclusion that crystals grown at any reasonable rate from the melt must have a mosaic

structure, and that an approximation to an "ideally imperfect" state is really the normal state of such a crystal.

It is to be expected that, for very slow rates of crystal growth, the space between the primary needles will be filled in with solid crystal almost as rapidly as the needles grow, so that the needles should be practically obliterated. We should, therefore, expect crystals grown very slowly from the melt to appear as smooth faced polyhedra. If the rate of growth of the primary and secondary needles is in excess of the rate of growth of crystals from the intervening melt, then the crystals should grow as dendrites. We should, therefore, expect a dendritic structure in crystals grown rapidly from the melt. Both these predictions are consistent with ordinary experience.

For most materials, even if large ideally perfect single crystals could be grown easily from the melt, they would probably not stay perfect. This may be illustrated by the case of some single crystals of copper grown by the writer from the melt in an atmosphere of hydrogen. The crucible containing the molten copper was lowered very slowly (0.005 inch per minute) through a vertical furnace two feet in length. Each part of the newly formed crystal was therefore kept very near to its melting point for a long time, thus giving it every chance to be as perfect as possible. Copper crystals about the size of a lead pencil, formed in this way, could hardly support their own weight when held horizontally from one end. The act of deformation changed the bent portion of the rod from a single crystal to a multitude of small crystals each having a mosaic structure.

The ease with which these single crystals of copper can be deformed is also shown by the following. The crystal axes of a somewhat larger specimen were determined by X-ray methods and the crystal was then slowly sawed by hand and carefully dressed up with a fine file so as to give it faces corresponding to the cube faces of the crystal. Care was taken throughout the whole procedure to keep from bending or deforming the specimen. Only light cuts were taken so that the distortion of the interior should be a minimum and so that there should be no appreciable temperature rise due to too rapid an expenditure of energy. After the cube faces had been put on the specimen in this way further X-ray tests were made to check the correctness of the faces. The surface of the specimen was found to be polycrystalline. The specimen had to be

etched off to a depth of $\frac{1}{16}$ inch before X-ray evidence could be found that the remainder was a single crystal. That the effect is not confined to soft metals like copper may be shown by the fact that before the writer could determine the orientation of a polished slab cut from a quartz crystal, it was necessary to etch off the thin polycrystal surface which had been formed by the polishing operation.

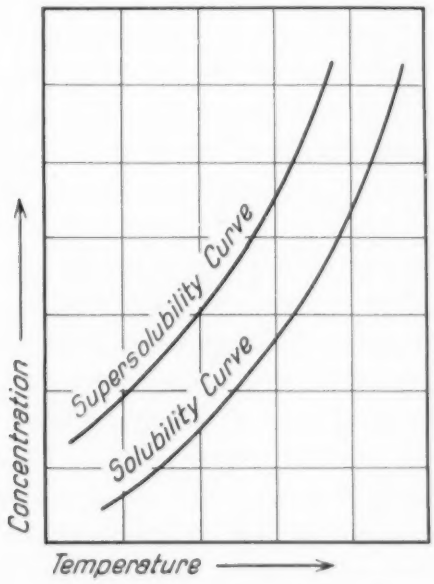


Fig. 1—Temperature - Concentration Diagram of a Typical Solution.

It is evident that only in the case of the most rigid materials can we hope to grow the melt approximations to "ideally perfect" single crystals and maintain them as such.

Probably the reason why the most perfect crystals reported in the literature are samples of diamond and calcite lies in the extraordinary rigidity of one and in the mechanical protection afforded the other by the conditions under which they grew. Most natural crystals either have grown under such conditions as to favor the mosaic type of structure, or have been subjected to geologic forces which have introduced imperfections by mechanical means.

(3) Growth from Solution—(a) Fig. 1 is a schematic temperature-concentration diagram for a typical solution. The solubility curve connects points at which "saturation" is found. If the temperature and concentration of such a solution are such as to give a point on the solubility curve, then a crystal of the solute suspended in the solution will neither grow nor dissolve. If the temperature

and concentration of the solution are changed to correspond to a point situated to the right of the solubility curve, the crystal will dissolve. If the temperature and concentration are made to correspond to a point at the left of the solubility curve, the crystal will grow at the expense of the solute in the solution. If no seed crystal is allowed to enter the solution, it may be cooled to a second temperature-concentration condition shown by the "supersolubility curve". Passing to the left of this curve, crystallization proceeds spontaneously and the crystals come down in the "labile shower", corresponding to the familiar "precipitate" of the analytical chemist.

The situation is exactly like that described for growth from the melt except that the presence of a solvent introduces the concentration of the solution as a variable along with the temperature. Bearing this slight complication in mind the theory of growth of crystals from the melt can be translated directly into a theory for growth from solution. The saturation curve connects freezing points of the solute at various concentrations. The supersolubility curve connects temperatures of maximum undercooling of the solute at various concentrations. Solution, therefore, becomes almost synonymous with melting, precipitation with freezing, and supersaturation with undercooling. In dealing with solutions, however, we cannot speak of the freezing point or melting point of the solute alone; we must regard the temperature of saturation as representing the freezing or melting point of the solute dispersed in contact with solvent in a solution of some definite concentration. We must similarly restrict our statements in connection with supersaturation.

There is every reason to believe that the mechanism of crystal growth from solution corresponds almost exactly to that described for growth from the melt. The growth of needles from the surface of the seed is, however, only an assumption in this case. The assumption is based on analogy with crystallization from the melt and does not necessitate needles large enough to be seen with the microscope. This picture leads us, then, to the conclusion that imperfection is the natural state for a crystal grown from solution, even when it is grown at a reasonably slow speed. Probably natural crystals of calcite, requiring thousands of years to grow, represent the closest possible approximation to ideally perfect crystals that can be grown from solution.

(b) We are accustomed to the fact that the unbalanced forces at the surface of a droplet of liquid have a component parallel to

the surface so that they tend to give the droplet a spherical shape. Even when the surface tension is very small, the surfaces of droplets of ordinary liquids are rounded because these liquids have no rigidity of shape. In the case of a crystal in contact with the melt, either the surface forces or the rigidity, or both, may have large values. If the strength of the crystal is in excess of the strength of the surface forces the crystal will be polyhedral in shape. If the strength of the crystal is less than the strength of the surface forces the crystal must have a rounded exterior. The interfacial tension between the solid and the melt does not necessarily decrease with tempera-

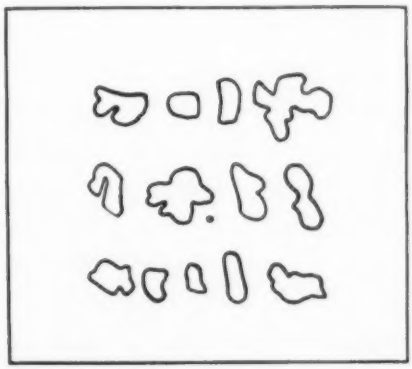


Fig. 2—Typical Rounded Outlines of Copper Crystals Grown from a Bismuth Solution at 800 to 900 Degrees Cent. Others May be Found on Page 31 of Reference 8.

ture at the same rate as does the strength of the solid material. The result is that in some cases the same material may assume a polyhedral or a spheroidal form depending upon the temperature at which the crystal is grown. In such cases the required freezing temperature may be obtained experimentally by crystallizing the material from a solution. For instance(10)(11) if copper is crystallized from a copper-bismuth melt containing 50 per cent copper by weight, most of the copper crystallizes out between 900 and 800 degrees Cent. (1650-1470 degrees Fahr.). If the melt contains only 25 per cent copper, most of the copper crystallizes out between 800 and 700 degrees Cent. (1470-1290 degrees Fahr.). Still lower concentrations of copper in solution in the bismuth crystallize out at still lower temperatures. The interfacial tension between the solid copper and the melt decreases so much more slowly with temperature rise than does the rigidity of shape that copper crystals grown from the 50 per cent solution all have rounded exteriors. (See Fig.

Table I
Effect of δ on Nature of $BaSO_4$ Precipitate

Equivalent Concentration of Reagents	P Expressed in Gms. Per CC.	δ	Nature of Precipitate
0.00005 to 0.00014	0 to 0.0006	0 to 3	No visible precipitate in a year. Micro-crystals expected after several years.
0.00014 to 0.0017	0.0006 to 0.0096	3 to 48	Slow precipitation at $\delta = 8$ Suspensoid stage at $\delta = 25$ Complete separation in months to hours.
0.0017 to 0.75	0.0096 to 4.38	48 to 21,900	Precipitation in a few seconds at $\delta = 48$ Instantaneous precipitation with crystal skeletons and needles at $\delta > 48$ At $\delta = 21{,}900$, crystals so small as to be barely visible.
0.75 to 3	4.38 to 17.51	21,900 to 87,500	Immediate formation of so-called amorphous precipitate.
3 to 7	17.51 to 40.9	87,500 to 204,500	Clear jelly.

2.) The 25 per cent solution yields a large number of copper crystals with polyhedral exteriors and a few with rounded exteriors. Still lower concentrations of copper yield nothing but polyhedral forms. Similar results may be shown by crystallizing beryllium from silver(12)(13), or aluminum(12)(14), or FeSi from iron(10)(15). Surface effects such as have been described will certainly increase still further the tendency toward a mosaic structure in a crystal grown from solution.

(c) Von Weimarn(16) has shown that the size of the crystals obtained by spontaneous crystallization from pure solutions is a function of the solubility, degree of supersaturation, and viscosity of the solution. Let S represent the solubility of the solute, let P be the degree of supersaturation (i.e. the number of gram-molecules of the solute which must be removed from one liter of solution to reduce it to saturation), and let η be the coefficient of viscosity of the solution. Then the perfection and particle size of the crystals of precipitate are determined by the "dispersion coefficient" δ, which is defined by the equation

$$\delta = \frac{P}{S\eta} \qquad (2)$$

When δ is very small, crystallization is very slow and the crystals would probably be very perfect. The time required to grow a sizable crystal would, however, probably be measured in geologic units rather than in hours or days. When δ is very large the number of

spontaneous nuclei is so great that practically the whole solute is in the form of nuclei and the mass forms a so-called amorphous jelly. This is illustrated in Table I which gives some of von Weimarn's results on $BaSO_4$ precipitated from mixtures of aqueous solutions of barium thiocyanate and manganous sulphate. The greater the degree of supersaturation, i.e., the faster the precipitation of solute, the more nearly do we approach the amorphous jelly type of precipitate. Since the amorphous jelly has almost none of the characteristics which we associate with a crystal we may make the generalization that the faster a solute is precipitated the less perfect the crystals will be. It would seem from Table I that even for reasonably slow speeds of crystallization in the laboratory, imperfection is the normal state of a crystal.

(4) Growth in Solids—(a) It is inconceivable that two crystals having different orientations should meet in the body of a solid without having at the interface a thin layer of molecules whose positions represent a compromise between the locations demanded by one of the crystals and those demanded by the other. This thin semi-disorganized layer is the crystal analyst's substitute for the "amorphous intercrystalline cement" which has been postulated by many metallurgists.[9] This conception of a semi-disorganized intercrystalline layer leads at once to a picture of the mechanism of the growth of a crystal in a pure solid at the expense of its neighbors. In order that crystal growth may occur in a pure solid it would be necessary for one of the crystals to align the molecules[10] of this intercrystalline layer according to the pattern set by its own orientation. This in turn would produce a new intercrystalline layer which would have to be formed at the expense of the less favorably oriented crystal. The molecules of this newly disorganized layer would then have to be aligned to conform to the pattern of the growing crystal, and the whole cycle would have to be repeated over and over again until the less favorably oriented crystal disappears.

In ordinary metallurgical practice it often happens that a mass of metal is heated to encourage crystal growth. It is not often that solid crystalline materials of this sort are pure enough for the simple mechanism which we have just described to repre-

[9]Since the potential energy of the atoms or molecules in such a disorganized layer must be greater than the potential energy of the systematicaily arranged atoms of a crystal, it is to be expected that etching reagents will, in general, strongly attack the intercrystalline boundaries. This offers at once a rational explanation for many of the facts of intercrystalline corrosion.

[10]In the case of most metals, the word "molecules" as used here, becomes synonymous with "atom."

sent the actual facts. We have seen that when substances crystallize from a melt, the "insoluble" impurities tend to collect at the intercrystalline boundaries. It is obvious that these impurities will tend to form a mechanical barrier to crystal growth(10). To form such a barrier the amount of impurity need be only an extremely small percentage of the total, for it only has to be well scattered through a thin layer at the crystal boundary. In terms of this picture, in order to enable a crystal of a material of ordinary overall purity to grow at the expense of its neighbors, two conditions must be fulfilled: (1) the intercrystalline boundary must be punctured in some way in order to bring pure crystals in contact with each other, and (2) the mass must then be heated above some characteristic temperature range such that the molecules in the punctured areas become mobile enough to align themselves in accordance with the demands of the crystal which is to grow. This is consistent with the ordinary metallurgical experience that crystal growth in metals is facilitated by hammering, swaging, or passing the metal between rolls, followed by heating the deformed metal above some characteristic temperature. Mechanical working cannot destroy or remove the impurities from an intercrystalline layer, it can only change the distribution of the impurities so that here and there the layer is punctured. The invading crystal, therefore, cannot advance along a continuous front, but must be thought of as sending out needle-like shoots or sprouts through the punctured portions of the intercrystalline layer. The spaces between these needle-like projections must be filled in as well as possible by re-aligning the molecules of the invaded crystal through growth from the sides of the needles. Such a picture is so nearly like that which we had for the growth of crystals from the melt that we feel justified in the conclusion that imperfection is the natural state of crystals grown in mechanically deformed solids. This conclusion is consistent with the ordinary experience of crystal analysts.

(b) Certain materials show allotropic forms, that is, they exhibit more than one crystal form, each one of which is stable over a definite temperature range. A familiar example is the case of high-purity iron which changes reversibly(17) from the body-centered cubic "alpha" form to the face-centered cubic "gamma" form at 908.5 degrees Cent. $\pm$ 2. X-ray examination fails to show any amorphous range between the high and low temperature forms of an allotropic material. This must mean that allotropic changes do

not require molecules[11] to move past each other. Small motions of translation, sometimes accompanied by motions of rotation of the molecules, must be sufficient to enable an allotropic substance to change from one of its crystal forms to the other. This condition appears to be always fulfilled. The case of alpha and gamma iron will serve to illustrate the point. It is well known that a body-centered cube may be considered as a face-centered tetragonal prism with an axial ratio of $\frac{1}{\sqrt{2}}$. The face-diagonal of the body-centered cube becomes the edge of the base of the face-centered tetragonal prism. The altitude of the body-centered cube is identical with the altitude of the face-centered tetragonal prism. Let us assume for the sake of simplicity that the iron has changed from the body-centered cubic (i.e., face-centered tetragonal) structure to the face-centered cubic structure without change in density. Let a_{fct} be the length of the edge of the face-centered tetragonal prism and let a_{fcc} be the length of the edge of a face-centered cube of the same volume.

Then $$\frac{a^3_{fct}}{\sqrt{2}} = \text{vol. of f.c.t. prism} = a^3_{fcc} = \text{vol. of f.c.c.,}$$

so that $$\frac{a^3_{fcc}}{a^3_{fct}} = \frac{1}{\sqrt{2}}$$

or $$\frac{a_{fcc}}{a_{fct}} = 0.89$$

So in going from a face-centered tetragonal prism to a face-centered cubic prism of equal volume, the base must shrink to 89 per cent of its original length, and the altitude must increase to $89 \times \sqrt{2} = 126$ per cent of its original height. These represent pure motions of translation of the order of 0.45×10^{-8} cm. and 0.75×10^{-8} cm. respectively. It will be seen from the published data on the "packing diameters" of atoms that these are respectively of the order of $\frac{1}{5}$ and $\frac{1}{3}$ of the diameter of the atomic domain of iron, and are therefore of the order of only $\frac{1}{5}$ and $\frac{1}{3}$ of the maximum value which can be assigned, crystallographically, to the diameter of an iron atom. Evidently any mosaic structure in the original crystal has a good chance of persisting in the new crystal. Indeed, there

[11]For purposes of brevity the word "molecules" will be used here to represent not only true molecules and the atoms of metals, but also ions such as the CO_3^- ion in calcite and aragonite, or the NH_4^+ ion in ammonium chloride.

should be a good chance that additional strains would form which would even cause new crystal boundaries so that the new crystals would, in such cases, be smaller in size than the old crystals. Such a break-up of crystals during allotropic change (as from gamma to alpha iron) is of common occurrence in metallurgy.

(c) In metallurgical work it frequently happens that substance B may be "dissolved" in solid solution in substance A above some definite temperature, but below that temperature individual solid phases separate out which are either A and the ionic compound $A_x B_y$ or a solid solution of B in A and a solid solution of A in B. This involves much greater atomic motion than the processes which we have so far considered. Obviously atoms of B can travel through the body of the metal only by taking advantage of interstices between the atoms of A. It cannot be assumed that the compound $A_x B_y$, as such, travels through the metal; the interstices between atoms of A are hardly large enough even at high temperatures. The effect of travel of $A_x B_y$ can, however, be obtained solely through the migration of B plus slight motion of the atoms of A. There is good reason for assuming all the atoms of B in a solid solution to be combined with A to form "molecules" of the ionic compound $A_x B_y$. It may be shown, too, that the apparent migration of $A_x B_y$ can be accounted for if we assume that when each B^- ion[12] migrates it returns the valence electron which it has borrowed from an adjacent atom of A on one side, and that it borrows a valence electron from another atom of A on the other side. Each ion of B^- is thus always a part of an ionic "molecule" of $A_x B_y$, but it is not always combined with the same A^+. In this way although only ions of B^- travel through the metal A, each one is at any instant a real part of some "molecule" of $A_x B_y$. If this picture is accepted, a discussion of the effect of migration of the B^- ion will, in general, serve to explain both the formation of crystals of $A_x B_y$ and the formation of crystals of solid solution A - in - B or B - in - A.

It is evident that if an ion B^- is to move from the left side to the right side of an atom (or ion) of A, (1) the heat motion must happen to cause all the atoms (or ions) of A lying to the right of B^- to move simultaneously away from each other, leaving a hole through which B^- can pass, and (2) at the same time the heat motion of B^- must happen to move it in the direction of the hole.

[12]This statement is worded in terms of B being the negative ion. The changes in wording when A is the negative ion will be obvious.

The number of accidental opportunities of this sort per second will decrease as the temperature is decreased, partly because the average motion of the atoms is slower, and partly because a smaller fraction of the openings formed will be large enough in diameter. If, in their random wanderings, two ions of B^- find themselves in the correct configuration with each other and with the ions of A to conform to the crystal structure of $A_x B_y$, then, if this configuration represents a decrease in the potential energy of the system, the configuration will tend to be stable enough to persist. If now a third ion of B^- migrates to the correct position with respect to the other two, the configuration tends to become still more stable. This process is repeated until a crystal of $A_x B_y$ is formed. It is not to be assumed, however, that this crystal will be "perfect". Its very method of formation involves the chance of atoms of A being inclosed as impurities in the crystal, thus causing local distortions which would give the effect of a mosaic structure. If the configuration of $A_x B_y$ does not represent a sufficient decrease in the potential energy of the system, ions of B^- will tend to migrate off until they happen to meet other ions of B^-. If the resulting crystal[13] of B represents a decrease in the potential energy of the system, the crystal will tend to be stable enough to persist and it will grow if other ions of B^- happen to migrate to it. Since the migration of both A and B will be haphazard, the crystal of B will not be entirely free of A. Stray atoms of A may become enclosed mechanically in the crystal of B. These will exist as ions of molecules of $A_x B_y$ so that what we have called a crystal of B is really a crystal of a "solid solution of A (i.e., $A_x B_y$) in B". Similarly, laggard ions of B^- will be left enclosed as $A_x B_y$ in a "solid solution of B (i. e., $A_x B_y$) in A". This picture is consistent with ordinary metallurgical experience. It may be shown that these dissolved ions will introduce enormous strains in the crystal. These highly localized strains can only result in a mosaic type of structure.

Secondary Crystal Structure

We have now discussed the various important methods of crystal growth and in every case we have come to the same conclusion, namely, that imperfection is the natural state of a crystal. We have seen that, for crystals grown from the vapor or from the melt

[13]When such energy conditions exist, then if two B^{--} ions meet, each must return its extra valence electron to A so that atoms of B exist in contact with each other.

these imperfections may be pictured as being due to the formation of a skeleton of needle-like growths which is later filled in with solid crystalline material.[14] We must now try to find, in the very nature of the crystalline state, (1) some reason for the existence of such a skeleton and what its probable spacing is, and (2) the effect of such skeletons on the physical properties of crystals.

(1) The Nature of the Skeleton Structure ("Pi" Planes)—We need first to satisfy ourselves that there are spots on the surface of a crystal from which growth may take place with comparative ease. The following line of reasoning will show that this is indeed the case. We have already seen that surface tension effects are present in crystals. Estimates of internal pressure and measurements on the surface tension of molten metals and molten salts at their freezing temperatures lead us to believe that these surface tension forces in crystals are very large. We have seen that these forces may even be large enough, under the proper circumstances, to force a crystal to abandon its polyhedral shape in favor of a spheroidal shape. The surface of a crystal must therefore be assumed to be under a heavy stress. It is inherent in the very nature of surface tension that this stress must decrease with the depth below the surface. Consider for purposes of illustration a minute seed-crystal of an alkali halide such as NaCl.[15] The surface tension must tend to bring the surface Na^+ and Cl^- ions closer together on the cube face, thus decreasing the lattice parameter at the surface. Evidently, the surface cannot contract as a whole, for since the effect decreases with the depth below the surface, the smaller lattice parameter of the top layer would bring, at definite intervals, an ion in the top layer directly above an ion of the same sign in the next lower layer. Such an impossible situation would be avoided if the surface were contracted in patches of substantially the same size, with crevices separating the patches. The linear size, L, of such a patch can be calculated by the method of Zwicky(18) as[16]

[14] We have seen that there is good reason for assuming this same picture to hold also for growth from solution. Growth from the solid comes into the present discussion only to a minor extent, for the original crystals in the solid were formed either from the vapor, or from the melt or from solution.

[15] The picture given here may be generalized so as to apply to a metal by assuming the valence electrons to occupy positions in the crystal structure. The positive metallic ions would correspond to the Na^+ ions and the valence electrons would correspond to the Cl^- ions. Considerable justification may be found in the literature for this sort of picture. Of course each substance will have its own characteristic dimensions for its crevices.

[16] These calculations are identical with those made by Zwicky (loc. cit.) in the course of a much less detailed discussion. The reader is referred to Zwicky's articles in the Physical Review and in the Proceedings of the National Academy of Sciences for a presentation of his point of view.

$$L = 100 \frac{a_o}{\gamma} \qquad (3)$$

where a_o is the length in Ångstroms of the edge of the unit-crystal of NaCl and γ is the per cent contraction in the lattice parameter at the surface. Zwicky has shown(19) that, when a crystal of NaCl is put under tension along its length, it suffers a lateral contraction which may be as large as 5.4 per cent (Lennard-Jones has shown(20) that the lateral contractions of all the alkali halides are of the order of 6 per cent). We will assume, therefore, that the stress perpendicular to the surface of our seed-crystal of NaCl is accompanied by a contraction, γ, at the surface of 5.4 per cent of the normal lattice parameter. Then equation (3) becomes

$$L = 100 \frac{5.6}{5.4} = \text{approx. } 100 \text{ A} \qquad (4)$$

That is, if the surface of a newly deposited film of crystalline NaCl is to avoid having ions of the same sign directly over each other, it must be broken up by crevices which are not more than 100 A apart. Since there is no reason why these crevices must be closer together, we will assume that they have a substantially regular spacing of 100A. Such a surface should be one possessing minimum free energy.

Crevices of this sort will extend into the crystal to a rather definite depth which we will assume to be that at which the surface tension effect is no longer detectable. This depth may be calculated for NaCl as follows(18). Let ϵ be the decrease in surface energy due to the contraction in one square centimeter of surface. Then if the area of a single patch is S, the decrease in energy associated with the contraction is $S\,\epsilon$. Let S' represent the area of surface in the crevice which is formed at the expense of the energy $S\,\epsilon$. Then, since the energy used up in making the crevice must come from the surface energy, we have

$$S\,\epsilon = S'\sigma$$

where σ is the surface tension of the NaCl. Calculation on the basis of the ionic nature of NaCl gives ϵ a value of about 220 ergs/sq.cm. The related value of σ for solid NaCl is found to be 156 ergs/sq.cm. as follows: $\sigma = 0.12 \frac{e^2}{a_o^3}$ where e is the electronic charge and a_o is the lattice parameter of the crystal of NaCl. Then

$$\sigma = 0.12 \frac{(4.77 \times 10^{-10})^2}{(5.6 \times 10^{-8})^3} = 156 \text{ ergs/sq.cm. at room temperature.}$$

For molten NaCl at 800 degrees Cent., σ = approx. 100 ergs/sq.cm. If we assume that the surface tension decreases uniformly with the depth below the surface, we have an average value $\frac{\sigma}{2} = 78$, so that 220 S must equal 78 S′. Within the precision of the calculations we may say that $S = \frac{1}{3} S'$. Now the length, L, of one side of a patch was found to be about 100 A, so that $S = (100)^2$ sq. A. Since there are four crevice-surfaces per patch, the total length of the crevice per patch is 4 L = 400 A. The area, S′, of the crevice-surface associated with each patch must, therefore, be S′ = 400 d, where d is the depth in Ångstroms of the crevice. Since S is approximately equal to $\frac{1}{3}$ S′, we have

$$(100)^2 = \frac{400\,d}{3}$$

so that d is in the neighborhood of 75 A.

We therefore have the picture that by the time a seed crystal of NaCl has grown to be several hundred atomic diameters across, its surface is covered with a square network of crevices which are approximately 100 A apart and about 75 A deep. Obviously the width of each crevice must be at least the "packing-diameter" of a Na^+ or Cl^- ion. This picture is perhaps too simple. It is not to be expected that these crevices will be entirely empty. Near the top we must expect to find here and there stray ions of Na^+ and Cl^- attempting to bridge across from one wall of the crevice to the other. There is no reason to suppose that these ions occur at any definite spacing with respect to each other, but wherever such a stray ion does exist its exact position will be determined by the electrostatic forces between it and its neighbors on the walls of the crevice. These stray ions, then, would act as poor attempts at bridges here and there across the crevices. They would give the crystal as a whole somewhat more strength across the crevices than if they were entirely absent.

In order to facilitate further discussion of the effect of these crevices, we will assume that the surfaces of the patches on the seed crystal all lie in a horizontal plane. At the center of each patch, the ions are pulled equally in all horizontal directions by the adjacent ions on all sides. As we go closer and closer to a crevice we finally reach a region where the electrostatic pulls are not exactly balanced; the total pull toward the crevice is less than the total pull toward the center of the patch. The horizontal inter-ionic spacing

will therefore be smaller and smaller the closer we come to a crevice and the potential energy between adjacent ions will therefore become less and less. Similarly on the surface of a crevice, the vertical inter-ionic spacings will be smaller and smaller the closer we come to the surface of the patch, and the potential energy must become less and less. Ions at the corners formed by the intersection of two crevices with the surface of the patch will have the least potential energy of all; they will be closest to their neighbors. As the seed crystal grows vertically it is to be expected, then, that growth will take place most readily at these corners, for the newly arrived ions will be most tightly held at such points. This should result in a primary crystal growth along a vertical needle-like skeleton, with a subsequent filling in on the surface of the patch. This filling in should occur most rapidly at the edges formed by the intersections of the crevices with the top surface of the seed crystal, because of the relative closeness of packing of adjacent ions along these edges. The central portion of the patch should be the last to be filled in. Obviously, a height will at last be reached such that a horizontal crevice will be formed to relieve the distortion along the surfaces of the vertical crevices. The argument in this case is identical with the argument which originally led us to assume the existence of vertical crevices,[17] with one exception. At the moment of forming the horizontal crevice, we have at each corner of each of the original patches a vertical needle extending above the general level of the patch. When the horizontal crevice is formed, these projecting needles should determine the orientation of the new crystal fragment which will grow above the horizontal crevice. The orientation of the new growth above the crevice will therefore differ from that below it only by reason of some small accidental tilting of the projecting needles at the time of forming the horizontal crevice.

We have, then, arrived at a theoretical picture of the growth of the NaCl seed crystal which requires the final "single-crystal" to be really a mosaic of crystal fragments, all having nearly the same orientation, and all having practically the same size and shape, and separated by crevices of substantially uniform spacing. Generalizing this picture so as to make it apply to other salts and to metals, we may think of the structure of a "single crystal" as being a lat-

[17] Since the horizontal distances between the original vertical crevices are about 100 A. and since our calculations have shown that the depth of a crevice is about 75 A, it is evident that the horizontal crevices from the four sides of a given patch will all meet, thus giving a continuous horizontal crevice.

tice work of points (such as is described by the Theory of Space-Groups) on which is superimposed a coarser structure represented by the crevices.[18] Following the terminology of Zwicky(18)(21), we will call the planes of the finer structure "p-planes" and the walls of the crevices which outline the coarser structure "π-planes." Since each crevice must have two walls, it is evident that π-planes must come in pairs. We may call the crevices π-crevices. Just as the spacing of the p-planes is a characteristic of the material of which the crystal is composed, so the spacing of the π-crevices must be a definite characteristic of the material.

It is not to be expected that the surface forces which we have so far considered are the only forces tending to form crevices in a crystal. For instance, we have neglected entirely thermal strains caused by the fact that the latent heat of solidification is given up at the surface of the growing crystal. This heat must be taken away mainly by conduction through the crystal itself, so that as the crystal is built up it is subjected to rather large local strains. These strains should tend to alter somewhat the orientations of the crystal fragments which compose the mosaic, causing slight irregularities in the walls of the π-planes and thus giving rise to "super-crevices." Zwicky has shown(22) that electrostatic considerations also point to the existence in a "single crystal" of a structure still coarser than that of the π-planes. The walls of these super-crevices we may call II-planes, and the super-crevices themselves II-crevices. The picture of π-planes and of π-crevices is almost entirely a theoretical picture. There is at present no direct experimental evidence of their existence and it is hard to see how there ever can be. Because of the changes in the density of a crystal from point to point along the edge (and faces) of the mosaic, and because of the small width of the π-crevices in comparison with the width of the mosaic units, X-ray diffraction from the π-planes (i.e., from the spacings of the mosaic units as a whole) should be of almost zero intensity. The only real indirect evidence for the existence of π-crevices lies in the intensities of the X-ray beams diffracted from the p-planes of crystals. It will be remembered that the data on the intensities of diffracted X-ray beams show that most crystals are almost "ideally imperfect." This imperfection of structure is, of course, consistent with the idea of π-crevices but does not require them to be regu-

[18] This type of picture is consistent with all the X-ray data on the degree of imperfection of crystals, and leads directly to the outstanding mechanical and crystallographic properties of crystalline materials.

larly spaced. There does seem to be considerable indirect evidence for the existence of Π-planes and Π-crevices. This evidence will now be outlined, using the assumption that the distances between Π-crevices are substantially equal. If this assumption is not made, the picture becomes somewhat less elegant but the conclusions to be drawn will not be seriously altered. In such a case the few changes in wording required will be obvious. According to Zwicky's calculations, they may have a spacing as large as 5000 A or possibly even 20,000 A, depending upon the material of which the "single crystal" is composed. Apparently the super-crevices whose walls constitute the Π-planes are of somewhat greater width than the crevices which we have called π-crevices.

(2) Consequences of π-Planes and Π*-Planes*—(a) From the standpoint of crystal growth no substance can be regarded as being really pure, for if an impurity is present only to the extent of a few parts per million it may still affect the crystal growth by concentrating on the growing surface. Most ordinary materials contain impurities in amounts ranging from a fraction of one per cent up to several per cent. We may imagine these ions (or atoms or molecules) of impurity to collide with the growing surface in exactly the same manner as the ions (or atoms or molecules) of the crystallizing material. The chemical bond between the impurity and the crystallizing material may be (1) weaker than, (2) equal to, or (3) stronger than that between adjacent ions (or atoms or molecules) of the crystallizing material. (1) If the bond is weaker, the impurity will have a greater chance of leaving the surface than will the ions (or atoms or molecules) of the crystallizing material. The impurity will therefore be present mostly in the form of material entrapped in the π-crevices, in the Π-crevices, or in the intercrystalline boundaries. Only a fraction of it will be left to foul the growing surface and retard crystal growth. (2) If the bond is practically equal, the impurity will enter into the structure of the p-planes after the manner of the alums. (3) If the bond is stronger, either the impurity will remain on the growing surface, fouling it so as to retard growth, or the impurity will leave the growing surface, taking with it that portion of the surface material with which it has combined, and in such a case it must tend to concentrate at the π-planes, at the Π-planes, and at the crystal boundaries.

When an impurity tends to deposit on the growing surface of

a crystal, deposition must occur most strongly near the corners and edges of the patches, for these are the places where the potential energy becomes least. But these are exactly the places which are, according to our picture, the regions of fastest crystal growth. In other words, an impurity tends to foul the growing surface in such a way as to retard crystal growth most effectively. If it were not for diffusion of the impurity from regions of higher to regions of lower concentration, there would be little chance of having any un-

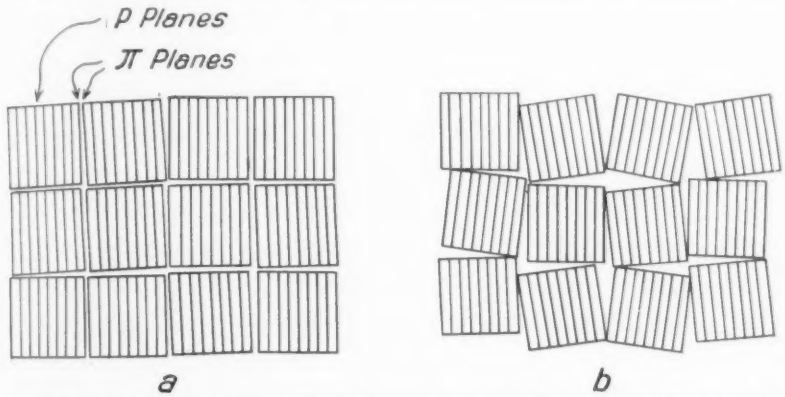


Fig. 3—(a) p-Planes and π-Planes in an Undistorted Crystal. (b) p-Planes and π-Planes in a Distorted Crystal.

fouled surface. When, however, the impurity adjacent to one group of patches is deposited on the growing surface, the region above that surface finds itself with a lower concentration of the impurity than its surroundings. The impurity at once tends to diffuse into these impoverished regions, thus reducing the chance of some other, adjacent, group of patches becoming fouled. These comparatively clean groups of patches, therefore, will be able to grow more rapidly than their fouled neighbors, thus forming macroscopic needles. Of course, since these needles tend to grow sideways as well as in the direction of their length, the sides become covered with patches separated by π-planes. A discussion similar to the above shows that the sideways growth will eventually become a matter of sending out secondary needles, and that these finally must send out tertiary needles, etc.[19] It may be assumed that all these macroscopic needles predicted by theory represent the actual needles described in the experiment with sodium hyposulphite. A similar line of reasoning may be applied to dendritic structures so familiar to metallurgists.

[19] This needle-like skeleton corresponds to the "lineages" of M. J. Buerger (*American Mineralogist*, *17*, 177, 1932) except that it is brought out in this discussion that the ultimate needles of which each large needle is composed can hardly avoid having transverse crevices. If the necessity for this complication is once granted, Buerger's "lineages" become identical with the needle-like skeleton described here.

(b) Consider an undistorted "single crystal" and let its apparent orientation be known from goniometer or X-ray measurements. It is a consequence of the mechanism of growth which we have described, that the individual fragments which compose the mosaic differ only slightly in orientation from each other. Any given set of atomic planes will appear to pass through one crystal fragment, across the π-plane, and through the next crystal fragment with hardly a perceptible break. This is illustrated in Fig. 3a. It may be assumed that for such a crystal, the orientation is also preserved across the boundaries of the II-planes. Such crystals may be expected to be mechanically weak. The large spacings between adjacent π-crevices and the still larger spacings between adjacent II-crevices will offer good opportunities for slip. Slip must occur first between the planes of greatest spacing, i.e., between the II-planes. This gives a reasonable explanation for the well known fact that in metals the slip bands have spacings which are rather exact multiples of the smallest spacing between bands. Since the direction of slip does not, in general, coincide with the direction of pull, torques will be set up which will tend to give somewhat different orientations to adjacent portions of the "single crystal." The II-planes would be pretty well wrecked and each portion of the "single crystal" would be jammed crossways against its neighbors. In a very real sense the original "single crystal" may be said to have been broken up into a large number of smaller ones. This is consistent with the ordinary experience of X-ray investigators. Slip must then take place between the planes of next greatest spacing, i.e., between the π-planes in each portion of the crystal. The torques set up will tend to rotate the fragments of which the mosaic is composed so that they will no longer look like Fig. 3a, but will be like Fig. 3b. Further slip can only take place between the p-planes. This is not likely to take place because of the closeness of the spacing. Before slip will take place between the p-planes, it is to be expected that rupture will occur along the line of the wrecked II-planes or π-planes.

If we adopt this picture of slip, we have not only explained at once why metals show block-slip rather than a continuous shear, but we have made it necessary for the block-slip to occur in small finite increments. The picture requires that slip must occur first between the two weakest II-planes. Slip will proceed until the planes become wrecked at some point by the jamming of the π-plane structure. Slip must then start in the next weakest II-crevice. This

process must continue until finally the process is taken up by the weakest π-crevices. In other words, slip must be a step-by-step process. Experiment shows that this is actually the case. Joffé and Ehrenfest and later Miss Klasson have shown(23)(24) that shear in zinc and in rock salt progresses in small jumps. The magnitude of the jumps remains constant to within 10 per cent for thousands of jumps. The initial time interval between successive jumps depends upon the difference between the applied load and the elastic limit, but for a given shearing stress it gradually increases until the jumps finally cease. The effect is illustrated in Fig. 4 which is taken from Joffé's, "Physics of Crystals" (McGraw-Hill, 1924).

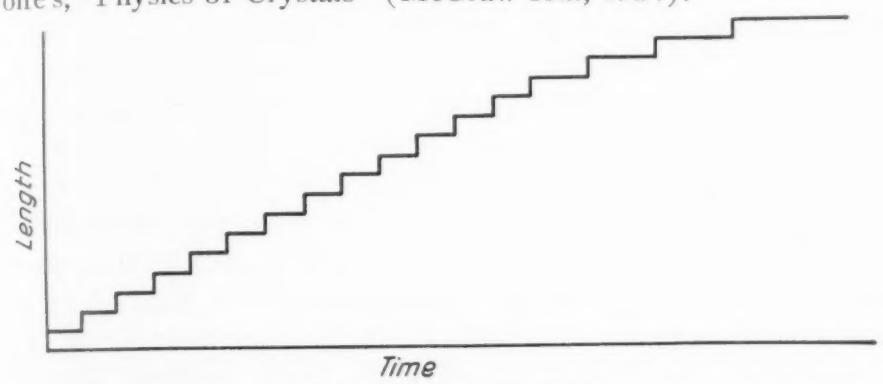


Fig. 4—Step-by-Step Slip.

It is well known that slip ordinarily occurs in the direction of those p-planes which have the greatest interplanar spacing. Our discussion of slip has therefore implied that the π-planes and the II-planes lie parallel to those p-planes which have the greatest interplanar spacing in the crystal. An examination of our discussion of the formation of π-planes shows that this is implied there too, for crevices may be expected to form most easily along the largest interplanar spacings of the growing crystal. This in turn implies that the normal direction of crystal growth is perpendicular to the slip planes in an orthogonal crystal. Cases in which growth appears to be in some other direction may really be examples of a zig-zag growth perpendicular to members of the family of slip planes.

Obviously, as the weakest II-planes and π-planes are wrecked in succession so that they can no longer slip, the tensile strength of the crystalline material must increase; that is, the crystal must strain-strengthen. The only way to avoid strain-strengthening would be to keep the material at such a temperature that the wrecked planes can repair themselves as a result of the high atomic mobilities as-

sociated with thermal agitation. The picture which has been given for the mechanism of slip explains strain-stiffening also, for Joffé has shown by X-ray methods(23) that when a single crystal is bent beyond the elastic limit it really suffers a large number of minute shears of the block-slip type. Since the tensile properties of materials are pictured as depending upon the Π-planes and π-planes, it is not surprising that the tensile strength of a crystal can not be calculated from the electrostatic forces between the ions in the p-planes. As would be expected, the actual tensile strength of a crystal is always considerably smaller than that calculated from the p-planes.

We have seen under (a) that next to the intercrystalline boundaries, the crevices between the Π-planes and between the π-planes offer the most favorable place for the deposit of impurities during crystallization. The idea may be expanded beyond the meaning ordinarily attached to the word "impurity." When, by reason of an appropriate thermal history, an alloy "precipitates out" a new phase, then this new phase will tend to collect at the crystal boundaries, and in the crevices between the Π-planes and between the π-planes, provided only that the atoms have sufficient freedom of motion to permit the necessary migration. The presence of the new phase between the Π-planes and between the π-planes must, of course, act to bridge over these crevices in an irregular fashion thus tending to tie the side walls together and making slip more difficult. This offers a simple and apparently adequate explanation of the strengthening of metals by the precipitation of a new phase. The effect of carbon in the strengthening of steels comes to mind at once as an illustration. Metallurgists will find many other examples in ordinary metallurgical practice.

(c) The theory has indicated that at the edges formed by the intersections of π-planes the molecules are especially close together, thus forming structures of minimum potential energy, and that the spacing, (and therefore the potential energy), between molecules increases as we go from the edges toward the center of a patch. Because of the lower potential energy, the melting point of the edge-portions must be somewhat above the melting point of the main body of the patches. When a crystal is brought just barely up to its melting point, we may assume that the bonding of the Π-planes is first loosened, but the structure can not melt down because of the rigidity of the blocks of which it is composed; the material merely becomes soft. Similarly it can not melt when the bonds between

the π-planes are loosened. Finally, the centers of the patches must melt out, leaving the edges of the patches to slough off without melting. A similar statement could be made of the edges formed by the intersection of the Π-planes. These unmelted "edges" correspond to the sloughed off portions mentioned in our discussion of the growth of crystals from the melt. We therefore have a theoretical explanation[20] of the experiments of Goetz (5) and of Traube and von Behren(6) which have already been referred to, and the experiments of Richards(8) in which it was shown that the whole material does not become a truly homogeneous liquid until a temperature is reached which is appreciably above the melting point. We also have a rational explanation for the results of Boydson(25), who found that the electromotive forces of oriented bismuth crystals do not disappear at the melting point, but continue until the "liquid" is heated appreciably above the melting point. Applications of the theory of sloughing to the ordinary melting operations of the metallurgical industries will be at once obvious to all metallurgists.

(d) The same considerations of potential energy that we have already used in (c) serve to explain the action of etching reagents. An etching agent must attack first the regions of highest potential energy. It must therefore attack readily not only the intercrystalline boundaries, but also the centers of the patches before it attacks the edges next to the π-planes and the π-planes themselves. Similarly we must expect that it will attack the Π-planes last. It is not surprising then, that strongly etched crystals will show etching pits. We may assume that the boundaries of the etching pits are parallel to the Π-planes and therefore to the π-planes and to the p-planes of greatest interplanar spacings. If this picture is granted, we have a theoretical basis for the technique of Honess(26) in determining crystal symmetries by means of a careful study of etch figures. Goetz(27) has found the etching pits of bismuth to be characterized by steps which are separated either by a definite spacing or by a simple multiple of that spacing. He finds this fundamental distance to be $1.4 \pm 0.2 \times 10^{-4}$ cm. Since this is the correct order of magnitude for the distance between pairs of Π-planes he has published his data as offering possible confirmation of the existence of a secondary structure in crystals. In the opinion of the author,[21]

[20] This explanation offers a somewhat different point of view from that given by Goetz, who apparently assumes that the sloughed off portions represent whole patches.

[21] R. B. Barnes (Phys. Rev. *43*, 82, (1933)) has shown by infra-red absorption measurements that if large crystals of rock-salt are made plastic by soaking in water and are then taken out and dried superficially, they contain considerable water in the interior. This water

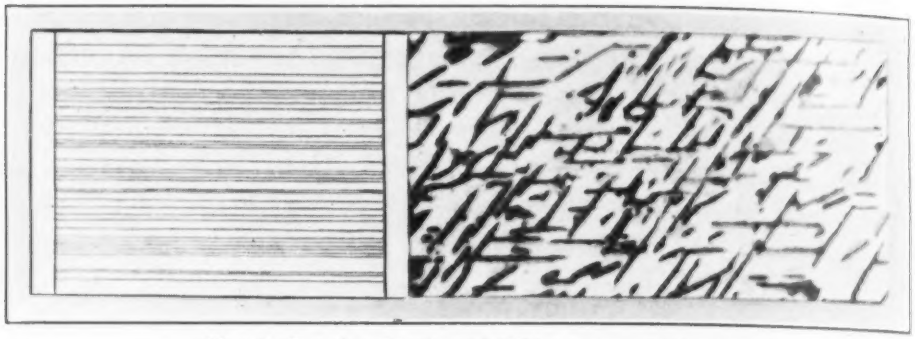


Fig. 5—Regular Spacing of Widmanstatten Figures.

Goetz' work offers one of the strongest pieces of direct experimental evidence in favor of the existence of Π-planes.

(e) We have already built up the picture, that when a new phase is precipitated in an alloy, it will tend to concentrate itself at crystal boundaries, and in the crevices between pairs of Π-planes and pairs of π-planes, if only the atoms have sufficient mobility to permit the necessary migration. If, however, the new phase finds that the crevices between the Π-planes and between the π-planes are already filled, then the new phase must crystallize as best it can in islands within the matrix. These islands correspond to the well known segregate structures of the Widmanstatten type. It has been pointed out by Mehl and his associates(28)(29)(30) that these islands are most likely to be formed so that some p-plane of the new phase lies parallel to a p-plane of the matrix having approximately the same interatomic distances. All the islands in a single crystal must therefore take the form of thin plates and must have the same orientation within the limits set by the mosaic structure. When the nucleus of such a crystal island is once formed, the region in its immediate neighborhood becomes impoverished with respect to the new phase. Migration will therefore occur from surrounding regions where the concentration is still relatively high.

Since the crevices between the Π-planes are already filled with other material, migration can not take place readily across the Π-planes. A somewhat similar barrier must exist between each pair of π-planes but because of the narrower width of the π-crevices the barrier will not be so difficult to overcome. We must expect, then, that migration toward the nucleus of each crystal-island will be limited to that portion of the new phase which lies within the volume

can be removed by heating for 24 hours at 150 degrees Cent. Different crystals showed this property to different degrees. If it could be shown by X-ray methods that the more permeable the crystal the more nearly ideally imperfect it is, we would have an excellent piece of direct evidence for the existence of Π-planes.

bounded by the nearest II-planes. There is therefore a very high degree of probability that there will be only one crystal island of the new phase in each of these volumes.[22] In other words, the average spacing between crystal-islands should be substantially uniform. It should be the same as the spacings between adjacent II-crevices projected in a direction perpendicular to the length of the crystal islands. Fig. 5 shows that these predictions are correct. Through the courtesy of the New Jersey Zinc Company, the photomicrograph is taken from the paper of Fuller and Rodda(31) on "Segregate Structures of the Widmanstatten Type Developed from Solid Solutions of Copper in Zinc." The photomicrograph was taken from a single crystal specimen whose plane of polish was such as to give symmetrical orientations of the Widmanstatten figures. Lines were drawn showing the planes of all the traces having a given orientation. Because of the small area of surface (less than 0.9 sq. cm) shown in the photomicrograph, it is not to be expected that every II-plane will be represented in Fig. 5 by a Widmanstatten line. It is evident, however, that the fundamental Widmanstatten spacings are all of substantially the same width and that the larger spacings are fairly exact multiples of this smallest width, as demanded by the theory. Calculations shows that their distance apart in the specimen is of the order of 5×10^{-5} cm. Because of the effect of the orientation of the plane of polish, and because of the mutual orientations of the planes upon which the segregated structures are found, only the order of magnitude of this distance is of any real significance. It is interesting to note that the spacing found here is of the same order of magnitude (one-third as large) as that found in Goetz' etching experiments on bismuth.

We have taken up systematically the experimental evidence as to the growth of crystals (1) from the vapor, (2) from the melt, (3) from solution, and (4) from the solid, and have discussed the physical conditions which are associated with each. In every case we found imperfection to be the natural state of a crystal. Following the general lines of the theory of Zwicky, we have built up in detail a theoretical picture of the growth of crystals such that the imperfections are inherent in the structure, and such that the ordinary properties of materials (such as manner of crystal growth, tensile properties, segregation of impurities, etch figures, and segregate structures of the Widmanstatten type) follow as corollaries.

[22] This is really a special form of the theory of rhythmic precipitation in which the limits of diffusion are set by the II-crevices instead of by the concentration of solute.

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DISCUSSION

Written Discussion: By N. A. Ziegler, Westinghouse Research Laboratories, East Pittsburgh, Pa.

Professor Davey should be complimented for his very interesting and remarkably clear description of crystal formation.

In our work of studying the magnetic properties of iron and its alloys, we are guiding ourselves by Yensen's working hypothesis which states that the only factor effecting magnetic quality is distortion of the space lattice, produced by (a) impurities, (b) mechanical strains, (c) strains at the grain boundaries.

All experimental evidence collected so far was in favor of this statement, and none against it. Professor Davey's statements give us another confirmation.

In attempts to produce materials with higher and higher magnetic properties, we succeeded in making and testing samples of unalloyed iron composed of very few large crystals and analyzing only infinitely small traces of foreign materials. Magnetic permeability of some of these samples was very high.

The best one had maximum permeability of /"max. = 220,000, and hysteresis loss of $W_{10} = 71$. According to Yensen's theory, further purification and elimination of the strains should still further increase /"max. and decrease W_{10}, causing them to approach infinity and zero respectively. So far it was hoped that with improvement of the technique these limits may be approached fairly closely, but Professor Davey's statements are somewhat discouraging. If, as he states, a certain amount of the distortion of the space lattice is an inborn property of the crystals, and cannot be eliminated by any treatment, then there must be a practical limit beyond which neither hysteresis nor maximum permeability can be improved, and perhaps we are not very far from it now. This by no means contradicts Yensen's theory, only restricting it to certain finite values, which remain to be determined.

The statement on page 979 " . . . . . the insoluble impurities tend to crystallize last, i. e., they tend to collect at the intercrystalline boundaries," is correct only providing that the freezing point of the impurity is lower than that of the melt. If reverse is the case, impurities will freeze first as spheroidal particles, much less harmful to the crystal growth than the intercrystalline films. I quite agree with Professor Davey that foreign materials are a serious obstacle for the grain growth and should be reduced to a very low figure in manufacturing of metallic single crystals (iron specifically). Even those elements which form solid solution with iron seem to restrict grain growth; so far crystals of 4 per cent silicon-iron or 50 per cent nickel-iron have not been grown to the size to which unalloyed iron has been grown.

Written Discussion: By K. H. Moore, Instructor in Physics, Rensselaer Polytechnic Institute, Troy, N. Y.

The paper is of great interest, throughout, Part I on the formation of inherently imperfect crystals being of particular interest in its hypothesis concerning grain growth, and the solution and the dispersion of "impurities" deliberately added to metals.

Part II, dealing with the secondary structure, as such, contains much pertinent data. Using calculations similar in form to those of Zwicky, the size

of mosaic "blocks" or surface patches in such heteropolar crystals as the alkali halides (NaCl) is approximated. Some doubt has recently been cast on the accuracy of Zwicky's calculations, and indeed, some rather incomplete experimental data do not check his approximations.

The value of the spacing of II-plane crevices is approximated at not much over 100 Å. While observing the diffraction of He atoms by the ionic lattice of LiCl, T. H. Johnson found indications of a diffraction pattern such as would be given by a crossed grating of a spacing much greater than the ionic. This evidence, however, was not resolved from the central, indiffracted beam. By carefully increasing the resolving power of the apparatus, the effect has increased, but the pattern was still unresolved. With the apparatus in use, the pattern given by diffraction from a grating of any spacing less than 235 Å would be separated from the primary beam. In this case, it was not; showing an effective spacing of the underlying phenomenon of very much greater than the calculated 100 Å.

The possibility of more than one secondary structure is quite apparent. Some work has been done at this Institute, concerned with measurements of one type of secondary structure, the results of which may be briefly stated.

For some time we have been interested in the possibility of observing the precipitation of a dissolved constituent in a metal, with the hope that precipitation would occur in such manner as to reveal the orientation and spacing of the precipitate. The system copper-beryllium was chosen, because of its great precipitation hardening. The addition of 2.5 per cent Be reduces the Cu lattice constant from 3.619 to 3.564 Å, thus giving a high probability of the formation of a secondary structure due to the strains set up during the changes in volume taking place in precipitation.

In addition to the expected favored precipitates at grain boundaries, a technique involving the use of plane polarized light revealed a network in the central matrices of the crystals. These were of regular orientation, reasonably complete, and in many cases the spacing was measurable. In the case of two such nets, of rectangular arrangement, the spacing was found to be $9.9 \pm 0.2 \times 10^{5}$ centimeters, using both dimensions. This spacing falls well within the predicted range for secondary structure of this character, comparing with the spacing of $1.4 \pm 0.2 \times 10^{-4}$ found by Goetz in bismuth, and the one of the order of 5×10^{-5} centimeters in alloys formed by the precipitation of copper from zinc by Fuller and Rodda.

Written Discussion: By Robert F. Mehl, Director Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh.

The history of the conception of a mosaic or secondary structure is a curious one. It originated in a suggestion made by Griffith some years ago in an attempt to explain the observed low strengths of glass fibers. Griffith postulated the existence of small cracks on the surface with resulting stress concentration resulting in turn in low strength. The great amount of research performed by Joffé and his colleagues in Russia and by Polanyi and Ewald and their colleagues in Germany upon the tensile strength of sodium chloride crystals in air and under water, led some inyestigators, especially Joffé, to explain the markedly low strength of sodium chloride crystals in air by the occurrence of

very minute cracks, following a reasoning much like that employed by Griffith.[1] Smekal in Germany was very active in studying the possible importance of microscopic cracks, but never postulated the regular mosaic type of structure. The main impetus to the conception of mosaic structures came from the theoretical work of Zwicky and the experimental work of Goetz, both in California.

Apparently the best experimental evidence for the existence of the mosaic structure is that obtained by Goetz[2], to which Professor Davey refers. This evidence cannot, however, be considered proof no matter how interesting and suggestive it may be. The other, that due to Bitter, Straumanis, etc., is too indirect to be very convincing.

The whole subject has recently become very active. Barnes[3] has shown this year that water actually enters into the sodium chloride crystal, apparently supporting Polanyi and Ewald that surface cracks have little or nothing to do with the low tensile strength in air. Smekal[4] afterwards quoted Orowan[5] in proof that Zwicky's calculations, advanced to show the necessity of a mosaic structure, are incorrect, and denied the validity of all suggested proofs for the existence of a mosaic structure. He states, "There is at present no theoretical or experimental support for the existence of a Zwicky secondary structure in rock salt. As far I can see the same situation holds for every other crystal. The beautiful results of Goetz with bismuth crystals are consistent with the existence of inhomogeneities which are not regularly distributed in the interior of crystals." With this statement a very hearty polemic began. Zwicky[6] replied defending his calculations and his belief in a mosaic structure, to which Smekal[7] replied with quotations from Zwicky in which the lack of experimental evidence was admitted and a strict mathematical proof admitted as impossible, and attempting to show that Straumanis' results in zinc and the results of etching and evaporation on other crystals could be explained in other ways. A few weeks ago Evjen[8] in California re-examined the mathematics of conditions of stability, concluding that an ideally perfect crystal could not exist, and that since salt crystals do actually exist, they cannot be perfect, and that the imperfection must consist in a Zwicky mosaic or secondary structure, quoting data on residual rays as experimental evidence for their existence.

The new evidence in favor of the existence for mosaic structure presented here by Professor Davey can hardly be admitted. When Professor Davey first presented this suggestion, during the February meeting this year of the A.I.M.E. in New York City, Dr. Charles S. Barrett of the Metals Research Laboratory in Pittsburgh offered a criticism which seems to me to be com-

[1] A. A. Griffith, *Philosophical Transactions*, Vol. 221A, 1921, p. 163-337.

[2] A. Goetz, *Proceedings*, National Academy of Sciences, Vol. 16, 1930, p. 99.

[3] R. B. Barnes, *Physical Review*, Vol. 43, 1933, p. 82.

[4] A. F. Smekal, *Physical Review*, Vol. 43, 1933, p. 366.

[5] E. Orowan, *Zeit. f. Physik*, Vol. 79, 1932, p. 573.

[6] F. Zwicky, *Physical Review*, Vol. 43, 1933, p. 765-766.

[7] A. F. Smekal, *Physical Review*, Vol. 44, 1933, p. 308-309.

[8] H. M. Evjen, *Physical Review*, Vol. 44, 1933, p. 491, 501.

plete, and I shall repeat it here with some additions. Fig. 5 in Professor Davey's paper shows a Widmanstatten figure developed in an alloy of zinc with a few per cent of copper, consisting of the ϵ phase precipitating from the solid solution of copper in zinc. This figure was analyzed by Fuller and Rodda[9] who prepared it, with the conclusion that the ϵ plates (the intersections of which with the polishing plane are visible in the figure) form parallel to the $\{10.4\}$ in the hexagonal zinc terminal solid solution. This photomicrograph is Fuller and Rodda's Fig. 3; the orientation of the plates is given in their Fig. 11. This latter figure shows that the directions which Professor Davey has measured are formed by the intersection of the plane of polish with two families of parallel plates approaching the surface at different angles. These two families form an angle of roughly 25 degrees with each other. Evidently then, the distance between the traces on the surface of polish in Professor Davey's Fig. 5 is entirely dependent upon the level at which the piece had been cut and polished: a different level would give a different inter-trace distance. It is evident that these distances and the unit distance determined can have no meaning.

The use of Widmanstatten figures as a method of attack is attractive on first consideration, but less so on further thought. These figures are not perfect; they vary in position and in angular disposition, so that frequency curves must usually be employed in studying the directions of the traces, and the promise of determining periods of spacing of the order of the postulated mosaic structure is not great. But more important than this, we find that Widmanstatten plates select different crystallographic planes for formation in lattices of the same type, and indeed from solid solutions in the same metal lattice; the compound Fe_4N precipitating from ferrite selects the $\{210\}$ plane whereas the compound Fe_3P selects an entirely different plane. To defend measurements on special disposition in such figures we should have to assume a widely varying choice of the π-plane, as determined by the type of element in solid solution. Furthermore we find that ferrite and cementite, preciptating from austenite select entirely different planes,[10] and in this case we would have to assume that changing carbon concentration affects the choice of the π-plane, or that the nature of the precipitate about to form determines the π-plane. These seem unlikely assumptions. Actually we find that the plane selected is determined by a unique choice between the lattice of the parent solid solution and that of the precipitate.

In view of all this it may well be questioned whether the evidence for the existence of mosaic structures is firmly established. It strikes me that the necessary thing in this work is the happy conclusive experiment, one free from the charge of indirectness to which all present reasons seem open. I have no prejudice against the idea of a mosaic structure, but I feel strongly that better experimental evidence is very much needed if mosaic structures are to be built into the theory of metals. Much that Professor Davey has said in this engaging paper may be taken as excellent evidence for the existence of imperfections in crystals, but not, I think, as unequivocal evidence for the existence of a mosaic structure. I suspect that he has assembled it in an endeavor to stimulate

[9]M. L. Fuller and J. L. Rodda, *Transactions*, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, Vol. 104, 1933, p. 116-130.

[10]R. F. Mehl, C. S. Barrett, and F. N. Rhines, *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, Vol. 105, 1933, p. 215-258.

discussion, however divergent from his own views, and I am happy to make my contribution.

Author's Closure

I am sorry that on page 15 of the preprint I failed to express the idea which I had in mind. I wish to thank Dr. Ziegler for calling my attention to this. I have made the changes in the final text necessary to express what I had in mind. I am not in agreement with the second sentence in his last paragraph, since I believe he has made too general a statement. As stated in the body of the article, I believe that the impurities will come out as spheroidal particles only when the surface conditions are favorable for such a state. I am greatly pleased with the information given in the last sentence of Dr. Ziegler's discussion. There is good reason to believe that a solid solution of A in B is really a solid solution of a compound between A and B. This means that there should be a tendency for the compound to form very minute crystals (smaller than can be seen under the microscope). Crystals of this sort should collect at the grain boundaries and in the II-crevices and should interfere with the growth of crystals of the solvent metal. The mechanism for this is given in the body of the article.

Dr. Mehl brings up the debate between Zwicky and Goetz on the one hand and Smekal on the other hand. This debate seems to center over whether or not the II-crevices are uniformly spaced in a crystal. As I have brought out in the final text of the body of the article, the result of this debate is not vital to the picture of the mechanism of crystal growth. The wording of the article has been chosen in terms of a uniform spacing of II-crevices since this yields a somewhat more elegant picture. The changes in wording required by a hit-and-miss spacing are obvious.

The new evidence for II-planes given in Fig. 5 is, of course, open to many possible interpretations. (Any single scientific fact should admit of an infinite number of interpretations.) From the point of view of II-crevices, each crystal island in a segregate structure derives its material from a volume bounded by adjacent II-crevices. The orientation of the island will be determined, as Dr. Mehl has shown, by a matching of interatomic spacings, but the *frequency* of the islands should be determined by the spacings of the II-crevices. The experimental fact of the regularity in spacings of these islands of segregated material lends considerable color to the picture of a uniform spacing of II-crevices.

In my paper I made no claim to consideration of the exact spacing of the Widmanstatten lines, because of the effects of the orientation of the plane of polish and of the mutual orientations of the planes of the solvent crystal in which the segregate structures are found. All I tried to call attention to was (1) the regularity of the spacing, and (2) the order of magnitude of the spacing. On these two counts alone is Fig. 5 to be considered as offering confirmatory evidence of the II-crevice picture as outlined in the body of the article.

ALLOYS OF IRON AND MANGANESE—PART IX

Transformations and Heterogeneity in the Binary Alloys of Iron and Manganese

By Francis M. Walters, Jr.

Abstract

This paper presents an experimental demonstration of the heterogeneity which may arise in the solid state when an alloy is heated into a two-phase region.

The iron-manganese alloys are particularly adapted to such a demonstration because the gamma phase transforms on cooling to alpha or to epsilon, depending on the composition. The formation of the alpha phase results in an expansion and the formation of epsilon in a contraction, hence these transformations may be identified dilatometrically.

While holding in the alpha-gamma region results in pronounced heterogeneity, homogeneity is restored by heating to 1000 degrees Cent. (1830 degrees Fahr.).

IT is generally recognized that considerable differences in composition in solid solutions are associated with the heterogeneous field, solid plus liquid. Evidence for these differences is found in the coring which results from cooling through the solidification range. That similar differences in composition may arise in the solid state in passing through a two-phase region, is less frequently considered. The binary alloys of iron and manganese may be made to exhibit striking differences in composition in the solid state by holding them within the alpha to gamma transformation range.

These alloys are particularly suited for such a demonstration because of the following characteristics. The epsilon phase, which occurs as a low temperature transformation product of gamma, has a composition range of 10 to 30 per cent manganese. (Fig. 2.) The decomposition of the gamma phase to epsilon is accompanied by a decrease in volume. This permits its identification dilatometrically

A series of papers presented before the Fifteenth Annual Convention of the society, Detroit, October 2 to 6, 1933. The author, Francis M. Walters, Jr., a member of the society, is associated with the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 21, 1933.

since the decomposition of gamma to alpha is associated with an expansion. Manganese does not diffuse readily, so that when composition gradients are established, they tend to persist. The marked hysteresis of the alpha-gamma transformation also helps demonstrate differences in composition, since a small difference in composition has a large effect on the temperature of the gamma to alpha transformation.

When an alloy of average composition A Fig. 1 is heated to a temperature T, just within the alpha plus gamma region, the gamma formed will have a composition B.

Thus when an iron-manganese alloy containing 7 per cent manganese is held at 600 degrees Cent. (1110 degrees Fahr.), the gamma formed will contain about 16 per cent manganese. Gamma of this composition transforms on cooling to room temperature, not to alpha, but to epsilon, so that a contraction on cooling the 7 per cent alloy after holding at 600 degrees Cent. shows that this temperature lies in the two-phase region.

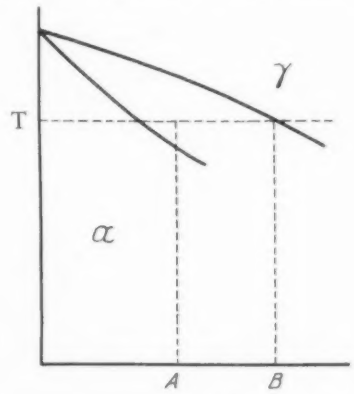


Fig. 1

Method of Investigation

Of the various methods used to study allotropic transformations, the dilatometric method is, in general, most easily interpreted, particularly when X-ray measurements of the phases involved are available. For example, in Fig. 4 (for the 10 per cent alloy) the discontinuity in expansion between 300 and 370 degrees Cent. (570-700 degrees Fahr.) (heating curve, A) is due to the transformation of a small amount of epsilon to gamma. The large contraction beginning at 600 degrees Cent. (1110 degrees Fahr.) and practically complete at 650 degrees Cent. (1200 degrees Fahr.) is the alpha to

gamma transformation. These conclusions follow from X-ray measurements which show that of the three phases involved, alpha has a larger atomic volume than gamma, and epsilon a smaller. On cooling, the gamma phase begins to change to alpha at 200 degrees Cent., and the fraction of alpha formed when the alloy has fallen to

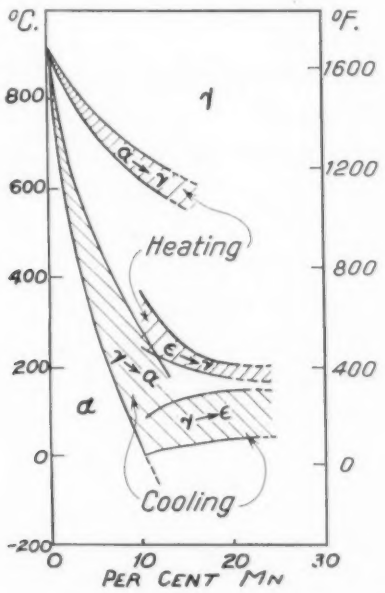


Fig. 2—The Boundary Lines of the Two-Phase Regions Were Derived from Dilatometric Observations with Homogenized Specimens.

a particular temperature may be deduced from the dilatometric observations. A correction must be applied to make allowance for the difference in expansion of the two phases. For example, about 65 per cent of the sample of curve A of Fig. 4 is involved in the alpha-gamma transformation and 5 to 10 per cent in the epsilon transformation. X-ray examination shows that a residue of gamma has remained untransformed.

The preparation of the alloys studied has been described elsewhere.[1] The 4.4 per cent manganese alloy contained 0.02 per cent carbon; the 7.2 and 10.4, 0.015 per cent carbon; and the 13.1, 0.03 per cent carbon. To reduce the heterogeneity of the forged alloys, the specimens investigated were held at 1325 degrees Cent. (2420 degrees Fahr.) for eight hours and quenched from 900 degrees Cent. (1650 degrees Fahr.). The soaking was carried out in purified

[1]Francis M. Walters, Jr., "Alloys of Iron, Manganese and Carbon. Part I. Preparation of Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 577.

helium at atmospheric pressure to lessen the sublimation of manganese.

That this treatment was successful in at least reducing the heterogeneity of the alloys "as forged" is shown by the narrowing of the temperature ranges of the transformations. For example,

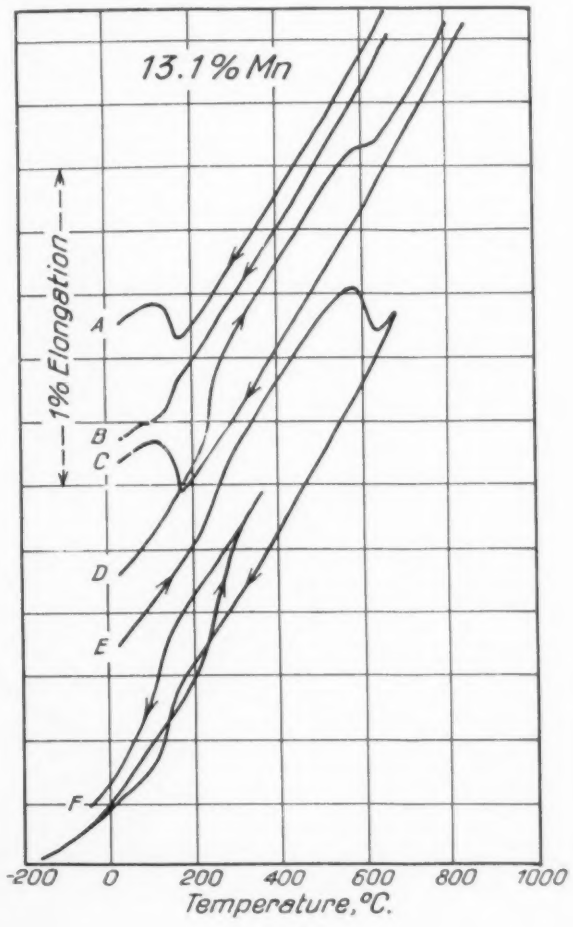


Fig. 3

the epsilon to gamma range decreased from 100 degrees Cent. for the 16.0 per cent alloy "as forged" to 10 degrees Cent. after the homogenizing treatment.

The dilatometer used has been described.[2] The observations were made at a pressure of 3 millimeters or less. Unless otherwise stated the heating rate was about 25 degrees Cent. a minute. The cooling rate was not uniform near room temperature, but the cooling

[2]Francis M. Walters, Jr., and M. Gensamer, "Alloys of Iron, Manganese and Carbon. Part IV. A Dilatometric Study of Iron-Manganese Binary Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 608.

program was repeated from run to run. The specimens were half an inch in diameter and one inch long. The change in length was observed with a dial gage, which was read to 0.00001 inch. Observations were made at intervals of 14 degrees Cent. or less.

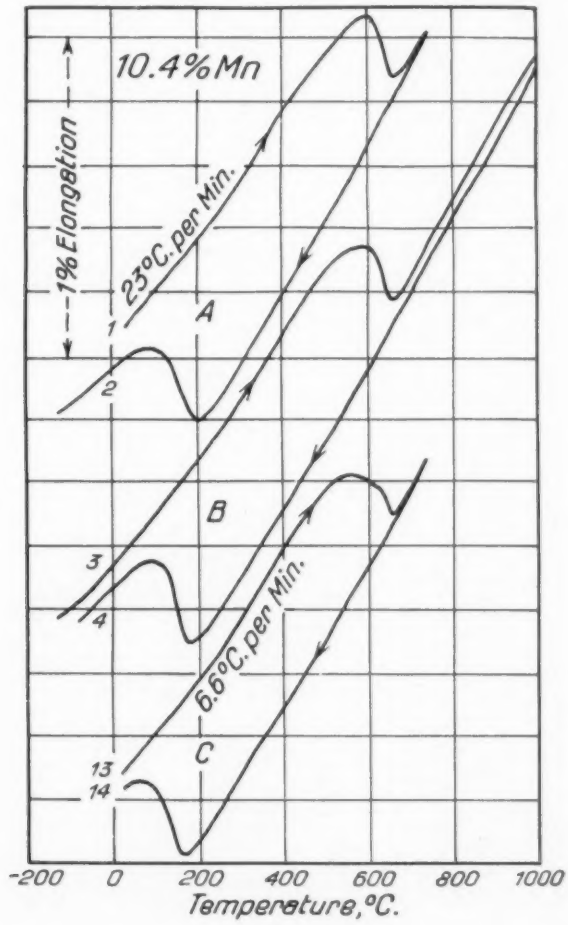


Fig. 4

Experimental Results

When a homogenized specimen of the 4.4 per cent manganese alloy is heated through the two-phase region, the alpha to gamma transformation is practically completed within narrow temperature limits (Fig. 7, curve 1). If the sample is heated only a little above the transformation temperature and cooled without giving an opportunity for diffusion, a second heating at the same rate as the first gives evidence of the setting up of differences in composition, even at such high rates of heating. (Fig. 7, curve 3).

These composition gradients can be made more pronounced if the sample is held in the heterogeneous field. On cooling from 722 degrees Cent. (1330 degrees Fahr.) the gamma which had been formed on holding for half an hour at this temperature was so high in manganese that its transformation temperature was lowered to

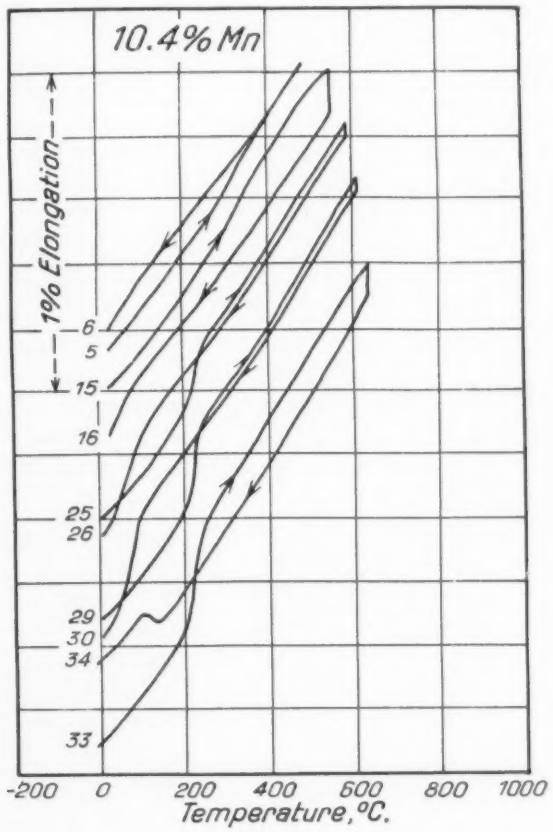


Fig. 5

370 degrees Cent. (700 degrees Fahr.), a temperature at which the transformation is nearly complete in a homogeneous specimen. Holding at 672 degrees Cent. (1240 degrees Fahr.) lowers the beginning of the alpha formation on cooling almost to room temperature.

If that part of the specimen which has transformed to gamma has become higher in manganese than the average composition of the alloy, then the rest of the alloy must have become lower in manganese. This is found to be the case, for on reheating (curve 19) the transformation temperature is raised. The "dispersion of composition" shown by the cooling curve 20 is marked, but heating the specimen to 980 degrees Cent. (1795 degrees Fahr.) (curve 21) and

holding at this temperature half an hour restores its homogeneity (curves 22 and 23).

On holding the 7.2 per cent manganese alloy at various temperatures in the heterogeneous range, the specimen showed an irreversible decrease in length which might be due to the formation of gamma at the soaking temperature (Fig. 6). However, on cooling from 648 degrees Cent. (1200 degrees Fahr.) a contraction was observed near

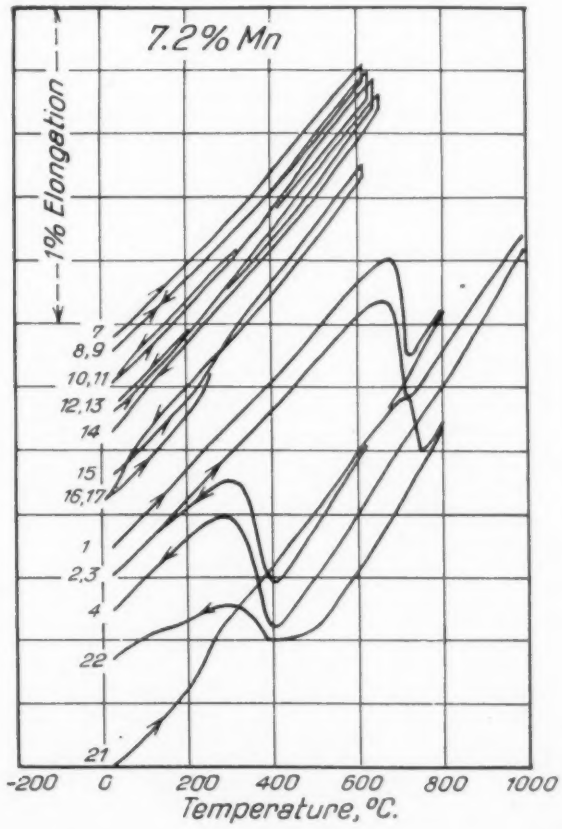


Fig. 6

room temperature which was sufficient to indicate definitely the formation of epsilon. The amount of epsilon formed was increased by holding the sample at a lower temperature, 611 degrees Cent. (1130 degrees Fahr.). The appearance of epsilon is taken to indicate that the part of the alloy concerned in the transformation was high in manganese. When the specimen in this condition was carried through the complete alpha to gamma transformation, the transformation temperature of the remaining alpha was raised. This shows that the untransformed part of the alloy had become lower in

manganese. From the shape of the subsequent cooling curve (22) it is seen that the homogeneity of the alloy had been seriously disturbed.

The curves of Fig. 4 show the "composition gradients" which develop in the 10.4 per cent manganese alloy even when fairly rapid heating rates are used. The alpha to gamma transformation was

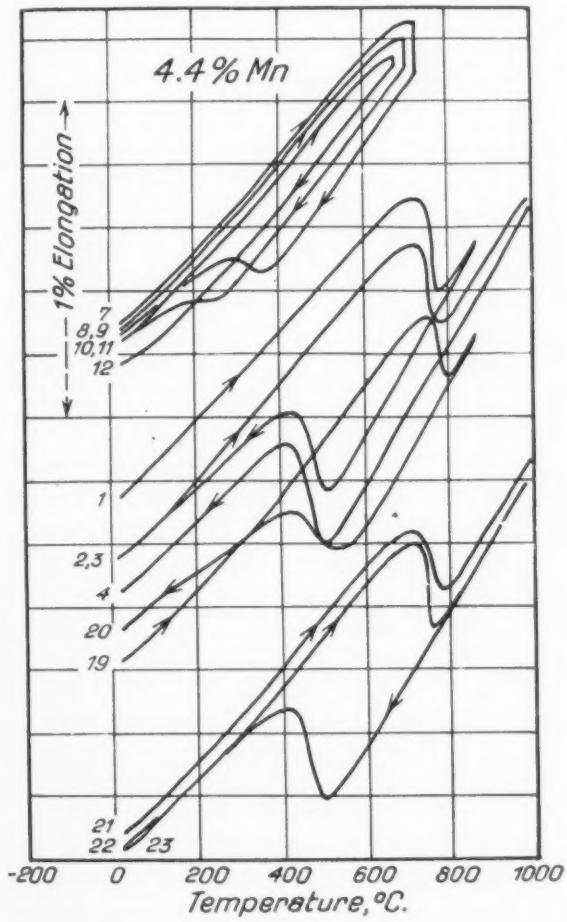


Fig. 7

much less sharp (curve A) after the homogeneous specimen had been heated through the transformation to 735 degrees Cent. (1355 degrees Fahr.) and cooled immediately. The effect is more pronounced with a heating rate as fast as 6.6 degrees Cent. a minute (curve C).

The amount of epsilon formed in the 10 per cent alloy at ordinary heating and cooling rates is small, as can be seen in curves 5 and 6, Fig. 5. Some gamma is retained in this alloy and part of the increase in length in curve 5 is probably due to the formation of

alpha from this gamma. When this alloy is taken to successively higher temperatures up to 610 degrees Cent. (1130 degrees Fahr.), held for half an hour and cooled, increasing amounts of epsilon are formed. At each higher temperature more gamma is formed which is high enough in manganese to go to epsilon on cooling. However, when the alloy is heated to 635 degrees Cent. (1175 degrees Fahr.)

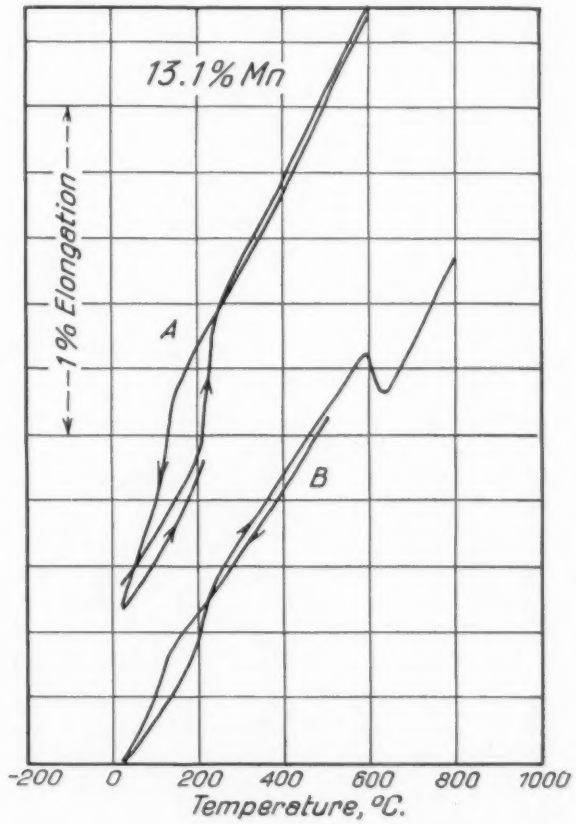


Fig. 8

and held, the gamma formed is low enough in manganese so that on cooling the transformation to alpha starts at 140 degrees Cent.

When homogeneous, the 13.1 per cent manganese alloy, under certain conditions, transforms principally to alpha. The specimen after homogenizing was cooled to 900 degrees Cent. (1650 degrees Fahr.) and quenched. When heated in the dilatometer, the magnitude of the alpha to gamma transformation indicates that there was a large amount of alpha present at room temperature following the quench (curve E, Fig. 3). When the alloy was heated to only 670 degrees Cent. (1240 degrees Fahr.) and cooled without loss of time,

the gamma decomposed principally to epsilon. The amount of alpha formed is shown by the heating curve D which is displaced from F. After the specimen is held at 1000 degrees Cent. (1830 degrees Fahr.) the decomposition is again mostly to alpha (curve 3). The character of the gamma decomposition thus depends upon the previous history of the specimen. Curve B followed a slow heating which was carried only to 670 degrees Cent. (1240 degrees Fahr.) while A shows that heating to 900 degrees Cent. (1650 degrees Fahr.) was almost as effective as heating to 1000 degrees Cent. (1830 degrees Fahr.).

None of the alloys studied except the 13.1 per cent showed a definite raising of the temperature of the start of the gamma to alpha transformation after having been soaked at 1000 degrees Cent. (1830 degrees Fahr.). When the alloy is homogeneous the beginning of this transformation should be at a lower temperature than when some dispersion of composition exists. This is the case in the 4.4 and 7.2 per cent alloys as is shown by a comparison of the cooling curves from 1000 degrees Cent. (1830 degrees Fahr.) and from just above the alpha to gamma transformation.[3]

To observe the effect of holding the 13.1 per cent alloy in the heterogeneous range the maximum amount of alpha was formed in the specimen by soaking at 1000 degrees Cent. (1830 degrees Fahr.). After holding at 500 degrees Cent. (930 degrees Fahr.) it was found that the amount of epsilon formed on cooling had not increased (curve A, Fig. 8). However, on heating through the alpha to gamma transformation it was found that the alpha to gamma transformation was smaller than when the alloy had not been soaked, hence some gamma had been formed at 600 degrees Cent. (1110 degrees Fahr.). Reference to the transformational diagram (Fig. 2) shows that the gamma formed at this temperature would be too high in manganese to transform on cooling.

Discussion of Results

When the homogeneous alloys are heated through the alpha-gamma range rapidly enough so that the dispersion of composition is not much increased, the transformation takes place within a fairly narrow temperature range. When sufficient time is allowed, differences in composition arise such that the transformation begins

[3]Cyril Wells has suggested that it is probable that in the 13 per cent alloy the determining factor is the perfection of the grains developed by the high temperature.

at a much lower temperature. In Fig. 2 the boundary lines of the alpha plus gamma region were derived from the dilatometric observations at a rapid rate of heating of homogenized specimens. The points below the curves indicate, not the lowest temperatures at which the alloys enter the heterogeneous field, but temperatures at which composition differences become sufficiently pronounced for demonstration.

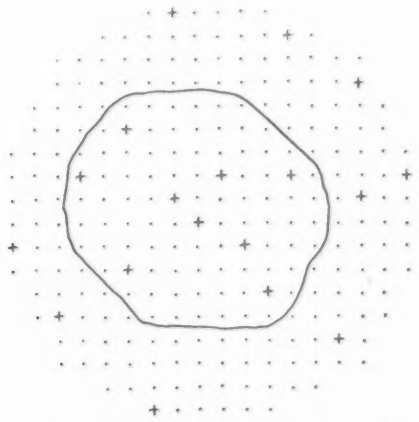


Fig. 9—The Dots Represent Iron Atoms, the Crosses Manganese Atoms in a 7 Per Cent Grain with a Random Distribution. Ten Per Cent of the Atoms Within the Closed Line are Manganese.

Just what should be taken as the alpha to gamma transformation range for an iron-manganese alloy of a given composition? The narrow range for the homogenized alloy is unsuitable because when the heating is fast enough to prevent the development of composition gradients it is not slow enough to complete the transformation at a given temperature. On the other hand, if the ideal of the transformation of a homogeneous specimen is abandoned, what limit is to be set on the procedure adopted to bring about composition gradients? Repeated heating to a particular temperature and holding for a short time produces a greater separation in composition, than holding for a longer time. The amount of epsilon formed in the 7.2 per cent alloy could not be obtained by heating to 611 degrees Cent. (1132 degrees Fahr.) and holding for a few hours, but was developed by first heating to higher temperature and then reheating to 611 degrees Cent.

It has been pointed out that manganese diffuses slowly in iron except at temperatures near the solidus and even at those temperatures several hours are required to bring about an approximately

uniform distribution. Differences in composition may develop on holding in the transformation range, even if the migration of the atoms is negligible. Consider a specimen of which every grain contains seven per cent manganese, but in which the distribution of manganese atoms within the grains is not uniform.[4] (Fig. 9). There will be points in a given 7 per cent grain where there is a sufficient concentration of manganese atoms to raise the composition at those points to 10 per cent. When a temperature of 620 degrees Cent. (1150 degrees Fahr.) is reached (the transformation temperature for 10 per cent manganese) the transformation to gamma will form new submicroscopic grains. On cooling, these minute high manganese grains retain their identity, unless heated to a temperature high enough for recrystallization.

While it is quite probable that homogenizing results in a random distribution of manganese atoms at the lattice points, even a regular distribution would be destroyed by the gamma to alpha transformation.

Summary

Dilatometric observations on the binary iron-manganese alloys revealed that large differences in composition may be produced in the solid state by holding these alloys in the alpha to gamma transformation range. An example is afforded of the usefulness of the dilatometer in the investigation of the transformational characteristics of alloys.

DISCUSSION

R. S. Archer: The relative absence or tardiness of oral discussion is scarcely surprising in spite of the importance of the subject. The same thing occurred in the presentation of the splendid series of papers on equilibrium conditions in the various aluminum alloy systems by Mr. Dix and his associates, and the reason is simply that there are very few able to say much about it. Perhaps only those who have done very careful work of a similar kind and usually in almost the same field, could comment on the theoretical part of the work.

I think it is obvious to all of us that this work has been carefully done, and is of a distinctly higher order than the constitutional work that was done not many years ago.

The remark that one of the authors made to the effect that the production of heterogeneity in the solid state seems unusual, calls to mind a more common

[4] R. F. Mehl and C. S. Barrett, "Studies Upon the Widmanstatten Structure I.—Introduction. The Aluminum-Silver System and the Copper-Silicon System," *Transactions*, American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, Vol. 93, 1931, p. 78.

occurrence of the same kind, essentially; that is, the precipitation of metallic compounds from solid solution, such as occurs quite regularly in the aluminum alloys.

If we quench an aluminum-copper alloy containing 4 per cent of copper from about 520 degrees Cent. we obtain a solid solution, and if we hold that alloy at 200 degrees Cent. for a period of time, heterogeneity results. The compound is precipitated and there is a change of volume and a change in resistance, although the precipitated phase is a compound rather than a solid solution.

From the practical standpoint, I wonder if either of the authors can relate any of the phenomena observed in their work to the reported occurrence of irregularity and occasional brittleness in the commercial steels containing say from 1 to 2 per cent of manganese?

C. S. Moody: I would just like to inquire of the authors if they have any data on some of the physical properties of these alloys, particularly with higher carbon content. Did I understand Mr. Archer to ask for examples of brittleness?

R. S. Archer: Cases have been reported, particularly in normalized steels, and I wonder if these various delayed transformations and heterogeneous structures—localized martensite, perhaps, could account for any of those properties. Mr. Moody did you have any cases in mind when you asked that question?

C. S. Moody: I did have something in mind but I do not know how closely it applies to the subject here today. My particular case is that of temper brittleness in the 1.75 per cent manganese steel. It is quite pronounced, I find in large sections. The pieces treated were cut from a normalized piece of 4¾-inch rolled bar 5 inches long. As treated the section had been cut to a cross section which was a right triangle with the hypotenuse the arc from the surface of the bar. The length was still five inches, and the weight of each was about five pounds. The analysis was:

Carbon	0.37 Per Cent
Manganese	1.73
Silicon	0.23
Phosphorus	0.019
Sulphur	0.029

One piece was oil-quenched from 1550 degrees Fahr. in oil, giving a Brinell 444, drawn at 1250 degrees Fahr., and slowly cooled; Brinell 217. A hardness reading on the Charpy bar when cut from the piece was Brinell 187.

A second piece was quenched and drawn with the above but quenched in brine from the draw. The Brinells were the same also except on the Charpy bar which was Brinell 196.

The other physical tests were as follows:

	Cooled from Draw	
	Fast	Slowly
Tensile Strength	105,950	101,900
Elastic Limit	75,500	73,700
Elongation Per Cent	27.5	25.5
Reduction of Area Per Cent	63.9	67.9
Charpy Impact Ft.-Lbs.	44.3	15.2
	45.4	13.3

The micrographs had fine carbide particles in a ferrite ground mass in both samples and showed very little difference in structure up to × 2000. The carbides when etched with picral as with nital always showed rougher in the brine cooled specimen.

I tried a 1450 degree Fahr. quench and found little difference. Different rates of cooling from the draw gave expected variations in the impact tests.

Mr. Honda's little article in METAL PROGRESS in which he discussed the carbides going into solution below the critical range was very interesting as bearing on this subject.

Author's Closure—By M. Gensamer

We have not studied the mechanical properties of our alloys because of the limitations of time and material.

With reference to the brittleness problem brought up by Mr. Archer, we can only call attention to the ease with which martensite forms in these alloys; that is, it is very easy to exceed the critical cooling rate in steels containing nearly 2 per cent of manganese. In view of this, it is not surprising that cases of brittleness in low manganese steels have been reported, and that the reputation of these steels has suffered through the lack of appreciation of the fact that they are slow reacting alloys.

Mr. Moody's problem is one that cannot be solved without experiment. We offer two suggestions. Rapid cooling (brine quenching) of a 5-pound piece with a sharp corner may result in severe residual stress concentrations, due entirely to the steep temperature gradients which must arise in cooling. Secondly, 1250 degrees Fahr. is a dangerously high drawing temperature for Mr. Moody's steel: he may very well have exceeded the A_1-lower transformation temperature, getting into the three-phase field containing austenite as well as ferrite and carbide. In this case he would certainly have found some martensite on quenching in brine, resulting in residual stress concentrations certain to lower the impact resistance of the steel.

ALLOYS OF IRON AND MANGANESE—PART X

Thermomagnetic Analysis of the Binary Alloys of Iron and Manganese

By F. M. Walters, Jr., and John F. Eckel

Abstract

The variation of magnetism with temperature was observed with a ballistic galvanometer. The effect of manganese on ferrite is to decrease its magnetism moderately. Alloys containing 16 per cent manganese and over are practically nonmagnetic, because the two phases of which they are composed, gamma and epsilon, are nonmagnetic.

Evidence, hitherto lacking, was found for an epsilon-alpha transformation.

Introduction

NO discussion of a ferrous system of alloys is complete without some discussion of their magnetic properties as a function of temperature; this paper gives the results of a thermomagnetic study of the binary alloys of iron and manganese.[1] The alloys used were prepared from vacuum-melted electrolytic iron and manganese purified by distillation, and were melted in chemically pure magnesium oxide crucibles in an atmosphere of purified argon.

Experimental Procedure

The specimens used for study were turned down from forged rods ½ an inch in diameter to ⅜ of an inch in diameter and were 6 inches long.

The furnace heating element of nichrome wire was wound noninductively around a quartz tube. The magnetizing coil consisted of 1869 turns of copper wire wound on a water-cooled brass tube 18 inches long and 3½ inches in diameter. A search coil of 30 turns

[1]Alloys of Iron, Manganese and Carbon, Parts I-IV, Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 577.

F. M. Walters, Jr., is associated with the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, and John F. Eckel is metallurgist with the Gulf Refining Co., Coraopolis, Pa. Manuscript received June 21, 1933.

was wound on the outside of the magnetizing coil and at its center. A small compensating coil was wound with the proper number of turns to give no galvanometer throw when no sample was inside the magnetizing coil.

Investigation of the distribution of the magnetic field strength along the axis of the coil showed the field to be uniform over the central 6-inch length where the specimen was placed. An impressed magnetizing force of about 100 gilberts per centimeter was maintained, however due to the demagnetizing effect of the short and thick sample used, the effective field strength was considerably less for the iron and the high permeability alloys.

The current in the magnetizing coil was kept constant and observations were made of the throw of the ballistic galvanometer produced upon reversal of the current. The period of the galvanometer was 25 seconds; with electrolytic iron the reversal of the current resulted in a throw of 23 centimeters on a circular scale 50 centimeters from the galvanometer. The samples were heated and cooled at a rate of about 7 degrees Cent. a minute. Observations were made at intervals of about 13 degrees Cent. A nichrome-constantan thermocouple was used with the bead imbedded in a saw-cut in the end of the specimen.

Results

The investigation was limited to (a) the manner in which thermomagnetic analysis revealed phase changes in the alloys studied and (b) the effect of heating into the alpha plus gamma field. No attempt was made to evaluate definite magnetic constants; these have been determined by Gumlich[2] for commercial alloys.

In the diagrams, the magnetic flux (observed as galvanometer deflection) is plotted against temperature. It must be remembered in connection with these diagrams that while the impressed magnetizing force was the same at all times, the effective magnetizing force, owing to the shape of the specimen, was a function of the magnetization of the specimen. The magnetic flux observed for iron was much less than if the specimen had been a ring or a rod very long in comparison to its diameter.

It may be seen from Fig. 1 that as the alloys increase in manganese, the magnetic flux becomes less and less until, with the

[2] E. Gumlich, "Über die Abhängigkeit der magnetischen Eigenschaften des spezifischen Widerstandes und der Dichte der Eisenlegierungen von der chemischen Zusammensetzung und der thermischen Behandlung," *Elektrotechnische Zeitschrift*, Vol. 40, 1919, p. 361.

apparatus used, no ferromagnetism was detectable with certainty in the 16 per cent alloys. Thermal hysteresis is pronounced in the alloys containing from 4 to 13 per cent manganese. The alloys are nonmagnetic above the Curie point for iron; that they are nonmag-

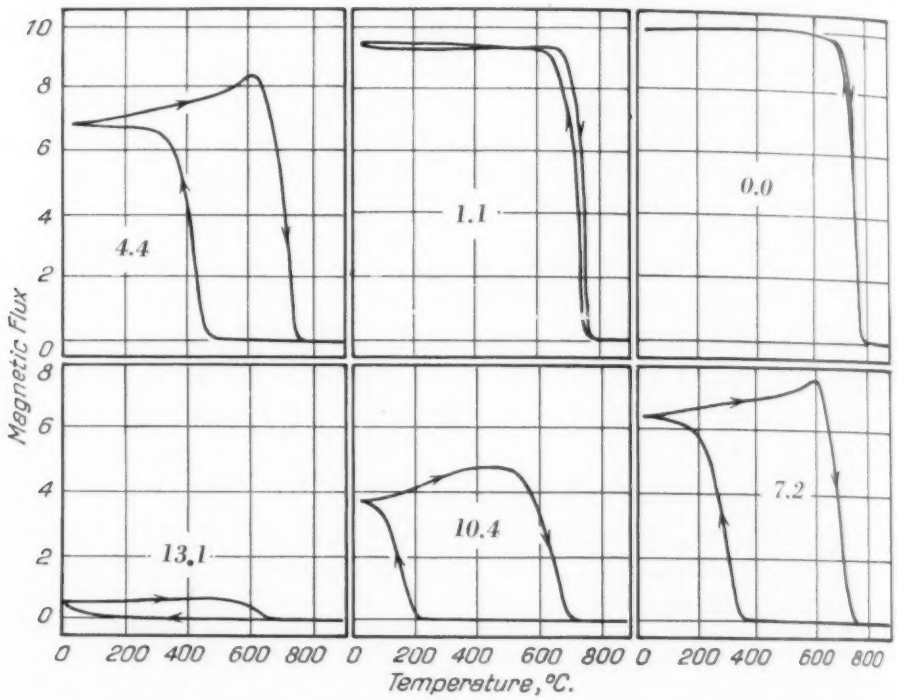


Fig. 1—Magnetic Flux-Temperature Curves for an Impressed Magnetizing Force of 100 Gilberts Per Centimeter.

netic also when in the gamma state, is shown by a comparison of the magnetic flux curves with dilatometric observations.[3] The 4.4, 7.2, and 10.4 per cent manganese alloys show a higher magnetic flux above room temperature than at room temperature. This phenomenon is observed in other ferrous alloys for certain magnetizing forces.[4] If the specimen is not heated to too high a temperature the flux-temperature curve is reversible.

The decided drop in magnetic flux shown by the 10 and 13 per cent alloys is due not only to the fact that some gamma (which is nonmagnetic) is retained at room temperature but also that in alloys of this composition part of the gamma phase transforms on cooling to the epsilon phase. The epsilon phase is formed from gamma on cooling at about 100 degrees Cent. and transforms to

[3]See Ref. 1.

[4]J. A. Ewing, "Magnetic Induction in Iron and Other Metals." London.

gamma on heating at about 300 degrees Cent. Since the 13 and 16 per cent alloys do not change magnetically at these temperatures, it is concluded that the epsilon phase is not ferromagnetic.

It has been demonstrated dilatometrically that holding the binary iron-manganese alloys in the alpha plus gamma heterogeneous field produces marked composition gradients. This effect is most pro-

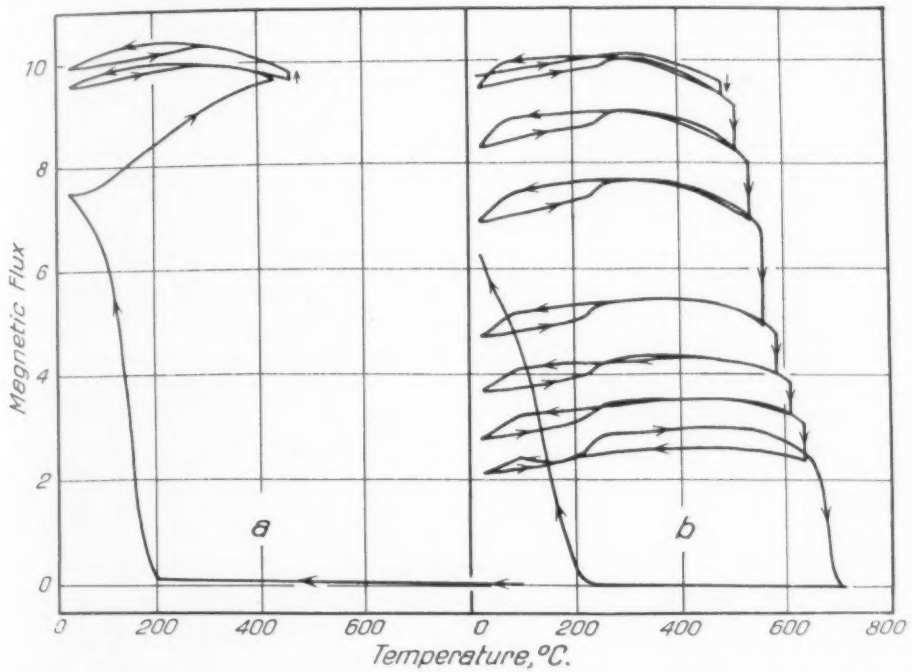


Fig. 2—Effect of Heat Treatment on 10.4 Per Cent Manganese Alloy (a) Cooled from 1000 Degrees Cent., and Held at Temperatures Which Caused an Increase in Magnetic Flux, (b) Held at Temperatures Causing a Decrease in Magnetic Flux.

nounced in the case of the 10 per cent alloy. Fig. 2a shows the magnetic flux as this alloy was cooled from 1000 degrees Cent. After heating to 430 degrees Cent. and cooling to room temperature, the magnetic flux has definitely increased. Holding at 460 degrees Cent. for half an hour slightly increased the flux. However, when the sample was heated to a slightly higher temperature (Fig. 2b) and held for half an hour a decrease was observed. With each increase in the temperature at which the sample was held, the magnetic flux was found to decrease. (The sample was held twice at 560 degrees Cent. for half an hour.) The decrease in magnetic flux at temperatures above 460 degrees Cent. is caused by the formation of gamma at these temperatures: this gamma is so high in manganese that it does not transform to alpha on being brought to room temperature.

An interesting feature of these curves for the 10 per cent alloy is the loss of magnetism between 100 degrees Cent. and room temperature on cooling and the increase between 200 and 300 degrees Cent. on heating. These temperature ranges correspond to those for the formation and disappearance of the epsilon phase. The results shown in Fig. 1 indicate that both gamma and epsilon are nonmagnetic. Hence it may be concluded that the changes of magnetic flux between 100 and 25 degrees Cent. on cooling and between 200 and 300 degrees Cent. on heating indicate respectively the transformation of some alpha to epsilon (a decrease in flux) and the transformation of epsilon to alpha (an increase in flux). This seems consistent with a peritectoid reaction[5] by which epsilon is formed from alpha and gamma.

[5]Suggested by R. F. Mehl at the Fourth Open Meeting of the Metallurgical Advisory Board, Pittsburgh, October 17, 1930.

ALLOYS OF IRON AND MANGANESE—PART XI

The Variation of Electrical Resistance with Temperature in Binary Alloys of Iron and Manganese

By F. M. Walters, Jr., and Cyril Wells

Abstract

The electrical resistance of binary alloys of iron and manganese containing between 0 and 29 per cent manganese was measured from 25 to 1000 degrees Cent.

It was found that manganese greatly increases the resistance and decreases the temperature coefficient of alpha iron. Manganese was found to have very little effect on the resistance of gamma iron, which at 1000 degrees Cent. is almost independent of the manganese content.

Introduction

THIS work is a part of a comprehensive investigation of the alloys of iron, manganese and carbon of high purity.[1] The alloys used were prepared from vacuum-melted electrolytic iron and manganese purified by distillation. They were melted under purified argon in chemically pure magnesium oxide crucibles. None of the alloys contained more than 0.03 per cent carbon and the other impurities were present in such small amounts they could not be estimated by the ordinary standard chemical methods.

Method of Measurement

The resistance was measured by the fall of potential along round specimen rods three-eighths of an inch in diameter. The current used was about 2 amperes and was measured by an ammeter which was read to one part in five hundred. The potential difference was observed with a Leeds and Northrup type K3 potentiometer. Temperatures were observed with a nichrome-constantan couple, the junction of which was inserted in a saw-cut in the specimen. The potential lead-wires were iron of the purity used for thermocouples;

[1]Alloys of Iron, Manganese and Carbon, Parts I-IV, Transactions, American Society for Steel Treating, Vol. 19, 1932, p. 577.

The authors are associated with the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 21, 1933.

these were pounded into saw-cuts about 5 inches apart. The observations were made with the specimens in vacuo, or when the observations required several days, in purified helium at atmospheric pressure.

Because of the large diameter and short length of the specimens, the fall of potential was small (0.4 to 5.0 mv.) even with a current of 2 amperes. The relatively large diameters (0.2 inch) of the current leads, made it impossible to keep the ends of the sample at the same temperature, and thermal e.m.fs. were developed which at times amounted to 10 per cent of the voltage measured. Accordingly it was necessary to reverse the current at each temperature at which observations were made.

Heating and cooling rates of about 6 degrees Cent. a minute were used and observations were made at intervals of about 12 degrees Cent. There was a constant difference of about 2 degrees Cent. between the temperatures at which the observations were made on reversing the current.

While the current was read to about one part in five hundred and the voltage to one part in several thousand, the individual observations were not so good as would be expected from this. Possible sources of error were variable contact resistance and ammeter bearings. Without special precautions in the preparation of samples, measurements of specific resistance have little significance and the agreement among the various alloys here studied is better than might reasonably be expected. The value of 10.1 microhm centimeters obtained for the specific resistance of vacuum-melted electrolytic iron is in agreement with that of other investigators. Yensen,[2] for example, obtained values from 9.91 to 10.25 for different samples of rather pure iron.

To measure the resistance more precisely, samples of much smaller cross section would be required. This would involve much greater care in the prevention of change in composition at high temperature as well as a more or less detailed study of the methods of producing wires from a series of alloys of widely varying mechanical characteristics.

Results

The results of the measurements on heating are presented graphi-

[2] T. D. Yensen, "The Magnetic Properties of the Ternary Alloys of Fe-Si-C," *Transactions*, American Institute Electrical Engineers, Vol. 43, 1924, p. 169.

cally in Figs. 1 to 3. In Fig. 1 the specific resistance in microhm centimeters is plotted against the temperature, while in Fig. 2 the resistances at various temperatures are plotted against the manganese composition. The data shown in Figs. 1 and 2 are from heating curves which followed a furnace cool from 1000 degrees Cent.

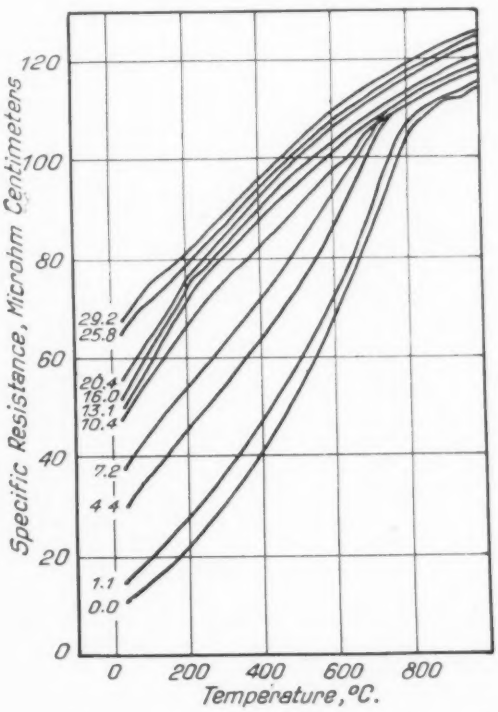


Fig. 1—Resistance-Temperature Curves for Iron-Manganese Alloys. For these Observations the Alloys had been Furnace-Cooled from 1000 Degrees Cent.

Manganese has a pronounced effect on the resistance when the alloy is in the alpha state (ferrite). One per cent of manganese increases the resistance of iron about 45 per cent. The temperature coefficient of resistance decreases with increasing manganese. The increase in the specific resistance of iron caused by the addition of 1 to 10 per cent manganese was found to be less than that reported by other investigators[3] whose alloys contained larger amounts of impurities.

When the alloys are in the gamma state (austenite), however,

[3]For example: W. F. Barrett, "On the Increase of Electrical Resistivity Caused by Alloying Iron with Various Elements," *Proceedings*, Royal Society (London), Vol. 69, 1902, p. 480-85.

Tokujiro Matsushita, "On the Influence of Manganese on the Physical Properties of Carbon Steels," Science Reports, Tohoku Imperial University, Series I, Vol. 8, 1919, p. 79.

manganese has little effect on the resistance. At 1000 degrees Cent. the resistance of the 29 per cent manganese alloy is only 10 per cent greater than the resistance of electrolytic iron at this temperature.

These results are in agreement with the generalization that the effect of an added element is to increase the specific resistance and to decrease the temperature coefficient of resistance; while a pure

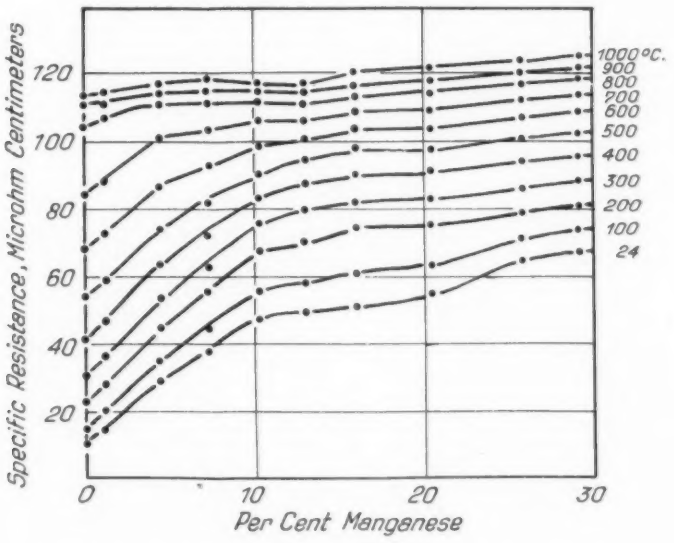


Fig. 2—Resistance Isothermal Curves for Iron-Manganese Alloys.

metal has a low resistance at room temperature, its resistance increases rapidly and at high temperatures approaches that of its alloys, since the alloys, although possessing higher initial resistances show a slower increase in resistance with temperature. Hence composition has a diminished effect at high temperatures.

The irregularities in the resistance above 900 degrees Cent. are probably due to the incomplete elimination of the effect of the thermal e.m.fs. developed between the iron lead wires and the specimens. The dip in the 1000-degree Cent. resistance-composition curve (Fig. 2) at 13 per cent manganese is probably due to experimental error in the dimensions of the specimen and forging defects.

In Fig. 3 are shown a few typical heating and cooling curves. The curve for the 4.4 per cent alloy displays the effect of the alpha-gamma transformation on the resistance. The resistance increases rapidly until a temperature of 760 degrees Cent. is reached, and the transformation from alpha to gamma is complete. The change in re-

sistance with temperature is much less when the alloy is austenitic. On cooling from 1000 degrees Cent. the alloy remains in the gamma state with its lower temperature coefficient of resistance, until a temperature of 480 degrees Cent. is reached, at which the gamma to alpha transformation begins. While the transformation is almost complete at 350 degrees Cent. it continues below this temperature

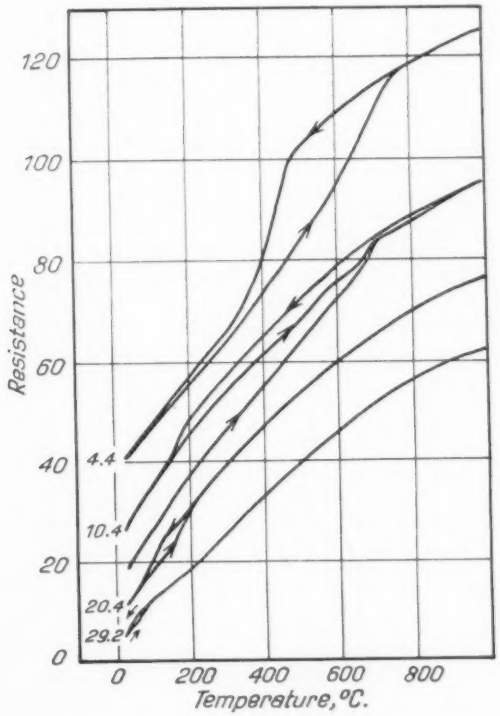


Fig. 3—Typical Heating and Cooling Temperature-Resistance Curves.

and the resistance on cooling is slightly higher than on heating, until room temperature is reached. The transformation range on cooling as revealed by the variations of resistance agrees very well with that observed dilatometrically, but the observations on heating fail to give any indication of the two-phase region between 700 and 800 degrees Cent. In Fig. 4 are shown dilatometric curves for alloys of the same composition as those for which the resistance curves are shown in Fig. 3.

The resistance of the alloys decreased when they were held in the alpha plus gamma field. This effect was most pronounced for the 10 per cent alloy, the resistance of which after repeated heatings into the two-phase region, was reduced to a minimum of 80

per cent of its resistance when cooled slowly from 1000 degrees Cent. The lower heating curve for the 10 per cent alloy in Fig. 3 is for the alloy after such treatment and the cooling curve shows the loss in conductivity following the heating to 1000 degrees Cent. This change

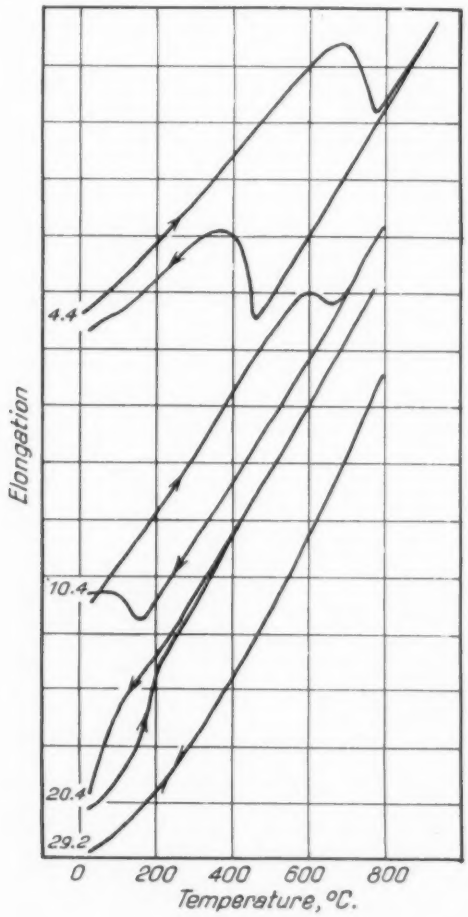


Fig. 4—Dilatometric Curves for Comparison with Resistance Curves of Fig. 3.

in resistance is due to the setting up of composition gradients which accompany holding in the alpha plus gamma field and which have been demonstrated magnetically and dilatometrically in these alloys. At the temperatures at which the alloy was held in the two-phase region, a small amount of high-manganese gamma was formed, and the manganese content of the remaining alpha was lowered so much that the resistance of the specimen as a whole decreased. In these alloys nothing was observed which would indicate that grain size

and strain had an appreciable effect on the resistance. The slow rate of cooling near room temperature, however, would tend to relieve any strains which might be set up.

The curve for the 20 per cent alloy is given to show the effect of the gamma-epsilon transformation on the resistance.

The amount of epsilon formed in the 29 per cent alloy is very small, and the thermal hysteresis is of the order of the experimental error. There is, however, a definite anomaly (between 25 and 200 degrees Cent.) in the temperature coefficient of resistance which corresponds in temperature to the irregularity in the thermal expansion of this alloy. This effect appears to be quite similar to the anomalous expansion of invar. Indeed, there is a marked similarity between the resistance-temperature curves for the iron-manganese alloys and those for the iron-nickel alloys,[4] not only for those alloys in which the alpha-gamma transformation occurs but also for those alloys in which gamma is the only phase at any temperature.

[4] G. Gossels, "Versuche über die Stabilität der Hysteresis Fe-Ni-Legierungen," *Zeits. anorg. allgem. Chem.*, Vol. 19, 1929, p. 182.

ALLOYS OF IRON AND MANGANESE—PART XII

Alloys of Iron and Carbon with 2.5 and 4.5 Per Cent Manganese

By M. Gensamer

Abstract

The 2.5 and 4.5 per cent manganese sections of the constitution diagram for the ternary system iron-manganese-carbon, with carbon up to 1.3 per cent, have been drawn from data obtained by the study of 12 alloys prepared with great care from materials of high purity.

Introduction

THIS study was undertaken as part of the program of the Metals Research Laboratory, formerly known as the Bureau of Metallurgical Research, at the Carnegie Institute of Technology on the ternary alloys of iron, manganese, and carbon. The general nature of this research has been discussed in earlier papers[1] of the series. It is sufficient to say that an effort has been made to prepare alloys of exceptional purity; although other papers on the iron-manganese-carbon system have been published, none has been on alloys of the purity used in this work. The results show that the recent study of Bain, Davenport, and Waring[2] on alloys of commercial purity are substantially correct—no important differences were observed between their results for alloys of commercial purity and the much purer alloys used for this study.

Preparation of the Alloys

The alloys were prepared from hydrogen-treated electrolytic

[1]Francis M. Walters, Jr., Cyril Wells, M. Gensamer, John F. Eckel, "Alloys of Iron, Manganese and Carbon," Transactions, American Society for Steel Treating, Vol. XIX, 1932, p. 577.

[2]E. C. Bain, E. S. Davenport, and W. S. N. Waring, "The Equilibrium Diagram of Iron-Manganese-Carbon Alloys of Commercial Purity," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 100, 1932, p. 228.

Based upon a thesis submitted by M. Gensamer to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of D.Sc. in Metallurgy.

The author is associated with the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 21, 1933.

iron, manganese purified by distillation, and charcoal prepared from sugar. They were melted in "C.P." magnesia crucibles under an atmosphere of purified argon.

The electrolytic iron was treated in purified hydrogen at a temperature of 1200 degrees Cent. for a sufficiently long time to decrease the sulphur and oxygen to amounts which were less than can be determined analytically. The principal impurity is copper, which is present in quantities less than 0.01 per cent. Before use, this iron was subjected to a vacuum treatment at a temperature well below the melting point to remove hydrogen.

Carbon was added in the form of iron-carbon alloys containing about 3 per cent carbon. These alloys had been prepared by melting Niagara electrolytic iron in C.P. magnesia crucibles with an excess of charcoal prepared from sugar. These melts were made under an atmosphere of natural gas shown by analysis to be free from sulphur. The manganese used was prepared by vacuum distillation of manganese originally produced by the thermit process.[3]

Forging and Homogenizing

The ingots were cut into quarters along planes containing the vertical axis of the ingot. One-quarter of each ingot was forged to a cylinder approximately one and one-eighth inch in diameter and three inches long before the homogenizing treatment. While this did not change the shape much, the quarter was severely worked by "upsetting" at least twice. The purpose of this forging treatment was to aid in securing homogeneity in the alloys. The forging was so carried out that the top and bottom parts of the ingot were at opposite extremities of the cylinder. In forging, the alloys were heated in a coke forge but were kept in the fire as short a time as possible. Before homogenizing, the surfaces of the forged cylinders were ground in order to remove the surface which might have been contaminated during forging.

The one and one-eighth inch diameter cylinders were homogenized, using an alundum boat as a support in an atmosphere of purified helium. Those alloys containing more than 1 per cent carbon were held about 12 hours at between 1065 and 1095 degrees Cent.; the

[3]James B. Friauf, "The Purification of Manganese by Distillation," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 1248.

alloys containing from 0.52 to 0.80 per cent carbon between 1150 and 1175 degrees Cent.; and the 0.18 carbon alloys between 1230 and 1260 degrees Cent. After this homogenizing treatment the cylinders were forged into one-half inch diameter bars. No evidence of coring was found in any of the alloys examined.

Sampling and Analysis

Both ends of each forged bar were sampled for analysis by turning off the whole cross section of the bar in a lathe, discarding $\frac{1}{16}$ inch from the surface. In order to machine the bars it was necessary to anneal them. This was done in a covered iron box

Table I

Chemical Analysis of Alloys

	Manganese				Carbon			
Identifying Mark	Dilatometer End	Opposite End	Diff. betw. the Ends	Average	Dilatometer End	Opposite End	Diff. betw. the Ends	Average
B	2.48	2.53	0.05	2.5	0.18	0.17	0.01	0.18
C	1.93	1.92	0.01	1.9	0.33	0.32	0.01	0.33
D	2.55	2.56	0.01	2.5	0.56	0.50	0.06	0.55
F	2.54	2.55	0.01	2.5	0.80	0.80	0.00	0.80
J	2.55	2.53	0.02	2.5	1.09	1.16	0.07	1.10
K	2.55	2.52	0.03	2.5	1.40	1.37	0.03	1.40
L	4.47	4.46	0.01	4.5	0.18	0.19	0.01	0.18
M	....	....	....	4.7	....	....	....	0.34
N	4.59	4.71	0.12	4.6	0.53	0.51	0.02	0.52
R	4.44	4.69	0.25	4.5	0.78	0.80	0.02	0.79
S	4.59	4.51	0.08	4.6	1.03	1.02	0.01	1.03
T	4.54	4.57	0.03	4.5	1.26	1.30	0.04	1.28

packed with steel lathe turnings and sealed with fine alundum cement. The box was put into a large gas fired muffle furnace at 785 to 800 degrees Cent. and held 1½ hours. It is unlikely that much contamination could occur at these relatively low temperatures. The temperature of the furnace was then dropped to 600 degrees Cent. and held for two hours, after which the gas was shut off and the box allowed to cool with the furnace.

Manganese was determined by electrolytic titration after oxidation with ammonium persulphate, and carbon by combustion. The materials used and the method of preparation of the alloys insured freedom from appreciable amounts of impurities. The results of the carbon and manganese determinations are tabulated in Table I.

Observations

To establish the sections of the ternary diagram each alloy was investigated with the dilatometer, and this was followed by heat treatments and observation with the microscope.

Dilatometer observations were made at very slow rates of heating and cooling in the critical ranges (1 degree Cent. per minute or less in some cases). It was found that the temperatures of transformation observed on cooling were much below the equilibrium temperatures as established by heat treatments, but that the transformation temperatures observed on slow heating were very little higher than the equilibrium temperatures, particularly for the hypereutectoid alloys. The low carbon alloys (0.18 per cent carbon) were more sluggish, and dilatometric observations made even at slow heating rates could not be depended on. It was demonstrated, however, that the dilatometer can be of use in such cases, provided extremely slow rates of heating are used. The beginning of transformation in an alloy which transforms very sluggishly was observed by bringing the specimen to a selected temperature, holding for a period, and then cooling, meanwhile observing the changes in length. Length changes on holding of the order of magnitude expected are not reliable criteria for transformation under these conditions, because of such extraneous factors as plastic flow in the sample. But if the reverse transformation is observed on cooling from the holding temperature, there can be no doubt that the temperature of transformation had been exceeded on heating. With this technique, dilatometric observations have been brought into good agreement with microscopic observations of specimens held for a long time at the proper temperatures. It is sometimes necessary to cool the sample well below room temperature in order to produce the desired reverse transformation by this method. This was necessary in the case of the 0.18 per cent carbon, 4.5 per cent manganese alloy, and is no doubt due to the fact that the first gamma phase to form on heating must be richer in carbon and manganese than the alpha phase from which it forms, and consequently transforms at a lower temperature.

Heat treatments were carried out in vacuum to avoid oxidation and decarburization of the samples. Forging scale was removed by grinding before heating. The temperature of the specimen was measured to within 3 degrees Cent. by a carefully calibrated thermocouple attached directly to the specimen. Experiments were car-

ried out to ascertain the length of time necessary to establish substantial equilibrium. It was found that the times necessary are less than those estimated by Bain, Davenport and Waring, which are conservative and applicable to alloys of higher manganese content. For the sake of safety, no times less than those estimated by these authors were used.

The A_{cm} point in a given alloy was determined by holding the alloy for a long period of time at increasing temperatures, quench-

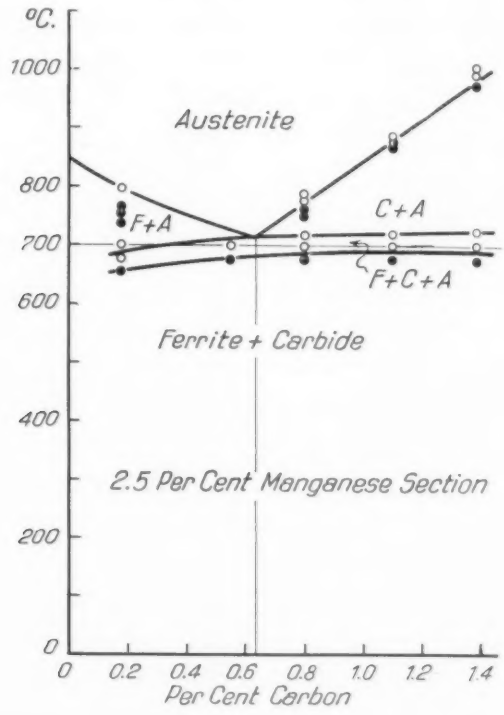


Fig. 1—2.5 Per Cent Manganese Section of the Constitution Diagram for the Ternary System Iron-Manganese-Carbon.

ing, and observing the microstructure. The A_{cm} point was taken as that temperature above which no carbides were visible under the microscope when etched with sodium picrate. An objective of 1.4 numerical aperture was used in the search for carbides.

The eutectoid transformation in these ternary alloys occurs over a range of temperatures; the lower temperature limit of this eutectoid range will be called A_1-lower, and the upper temperature limit A_1-upper. To determine the A_1-lower point, quenched samples were etched with nitric acid in alcohol; samples quenched from above

A_1-lower contained a dark etching constituent, tempered martensite, which was absent from those quenched from below A_1-lower. For A_1-upper in the two alloys of 0.18 carbon content, specimens were etched in sodium picrate; absence of carbides was taken as evidence that the sample had been held above A_1-upper. For A_1-upper in the

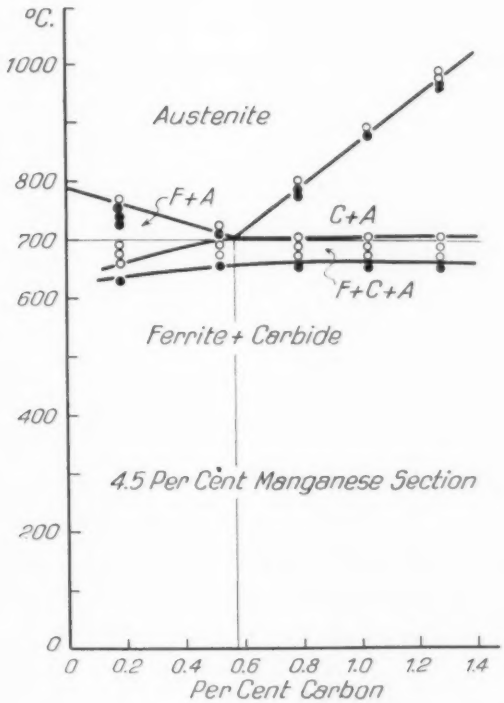


Fig. 2—4.5 Per Cent Manganese Section of the Constitution Diagram for the Ternary System Iron-Manganese-Carbon.

hypereutectoid alloys the dilatometric observations were relied upon; here the dilatometer proved perfectly trustworthy, and microscopic searching for ferrite areas unreliable. A_3 for the 0.18 carbon alloys was also determined with the dilatometer.

2.5 and 4.5 Per Cent Manganese Sections of the Ternary Diagram

From data collected in the ways just described, Figs. 1 and 2 have been drawn for the 2.5 and 4.5 per cent manganese sections of the constitution diagram for the ternary system iron-manganese-carbon. Such sectional diagrams are too familiar to need explanation, although one word of caution may perhaps be required. It

is impossible to tell from such a diagram the concentrations of manganese or carbon nor the relative amounts of phases in a heterogeneous field. For instance, the gamma phase formed on heating a low carbon alloy to just above A_1 is certainly much higher in manganese than the alpha from which it is formed, and is, consequently, of different carbon content than that indicated for eutectoid composition on the diagram, because of the changing solubility of carbon in the gamma phase with change in manganese.

According to Arnold and Reed[4] the manganese content of the carbides should be about 11 per cent for the 2.5 per cent manganese alloy, and about 20 per cent for the 4.5 per cent manganese alloy; this further complicates any effort to estimate the composition of the phases present in any part of the diagram. From a practical point of view this is not important; the useful information is the temperature and composition limits of the various fields of the diagram.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. F. M. Walters, Jr., and to Dr. V. N. Krivobok, under whose joint direction the work was carried out, and his appreciation of the interest in this work taken by Dr. R. F. Mehl, Director of the Metals Research Laboratory at the Carnegie Institute of Technology.

[4]Arnold and Reed, "Chemical and Mechanical Relations of Iron, Manganese, and Carbon Alloys," *Journal*, Iron and Steel Institute, Vol. 38, 1910, p. 169.

MARTENSITIC GRAINS IN AIR-COOLED LOW CARBON STEEL AND THEIR EFFECT ON MACHINABILITY

By O. W. McMullan

Abstract

This paper describes the occurrence of grains of martensite or martensite and austenite in air-cooled low carbon steels of fairly low alloy content. Their effect on cutter life and quality of finish on machined parts is discussed. A heating and cooling cycle is described which will eliminate both the martensite and banding which occur during treatments usually given.

Appearance and Properties

THE presence of martensitic grains in air-cooled low carbon steel was first noticed in a heat of open-hearth S.A.E. 4615 steel of the following analysis: C, 0.17; Mn, 0.45; P, 0.015; S, 0.030; Si, 0.26; Ni, 1.76; Mo, 0.27. This steel had given trouble in machining in an automotive gear plant after normalizing in a pusher type furnace. Some of the blanks were sent back to the mill where they were retreated by holding three hours at 1800 degrees Fahr., and cooled to 1200 degrees Fahr. at the rate of 100 degrees per hour, after which they were cooled in air from 1200 degrees Fahr. The first piece machined ruined the cutter. A small sample after the latter treatment was examined microscopically but none from the first treatment was available.

The microscopic examination revealed a considerable number of grains and parts of grains, which were structureless after short etching in nital. Deeper etching developed a faint needle-like structure typical of martensite in a background of austenite. Magnifications of 500 diameters or over were necessary to show the needle formation. Some of the areas occurred as isolated grains, but most of them were parts of pearlite grains, some at boundaries and others enclosed within the pearlite. The pearlite in steel of this analysis is granular rather than lamellar. Figs. 1 to 5 taken at 2000 diameters

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The author is metallurgist with the Timken-Detroit Axle Co., Detroit. Manuscript received July 28, 1933.

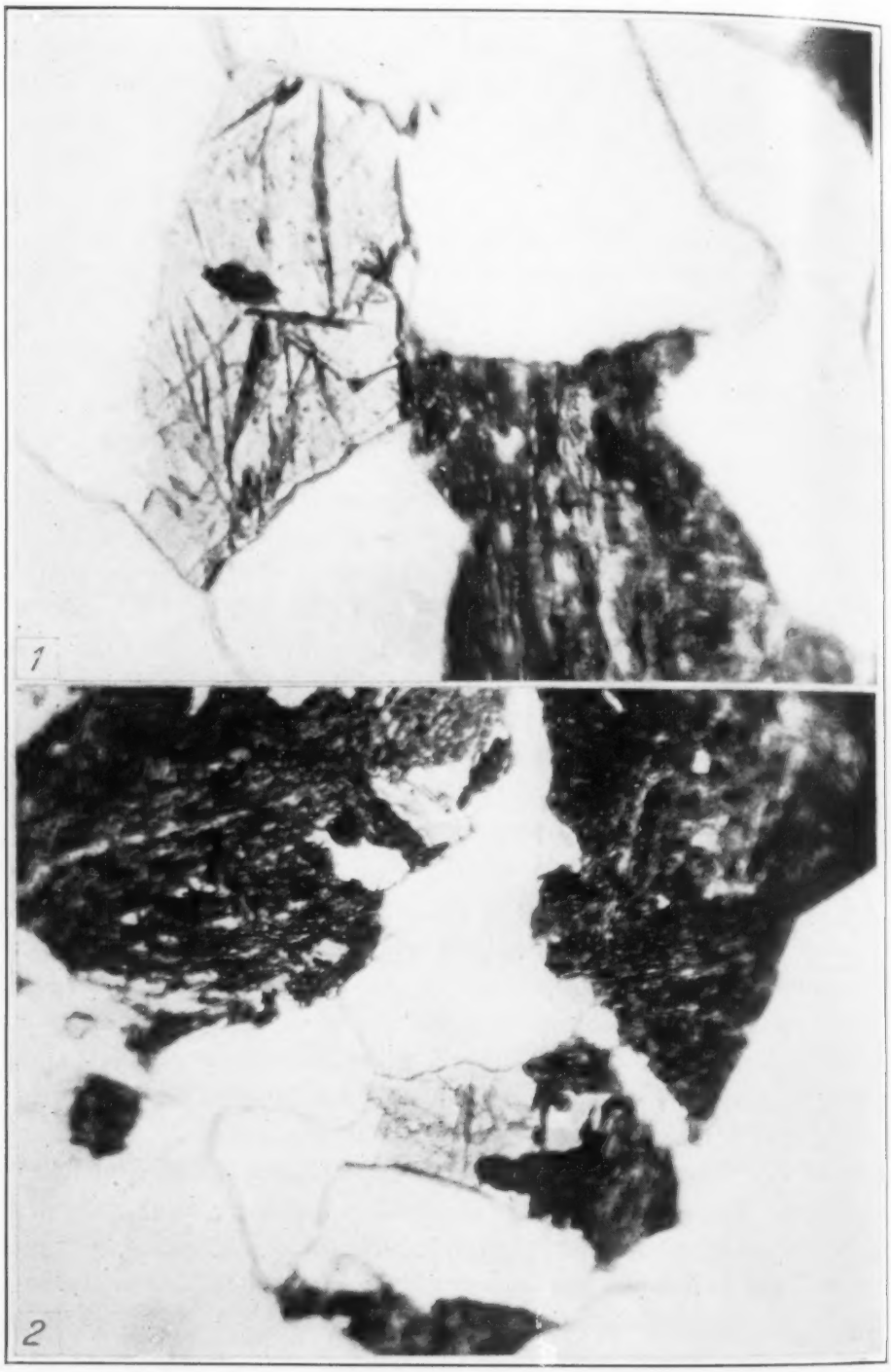


Fig. 1—S.A.E. 4615 Held at 1800 Degrees Fahr. for Three Hours and Cooled in the Furnace at the Rate of 100 Degrees Per Hour to 1200 Degrees Fahr., and then Air-Cooled. A Single Complete Grain of Martensitic Needles in an Austenitic Matrix is Adjacent to a Pearlite Grain. × 2000.

Fig. 2—Same as Fig. 1 but Showing One Half of a Grain of the Austenite-Martensitic Structure with the Other Half Pearlitic with Surrounding Grains Mostly Pearlitic. × 2000.

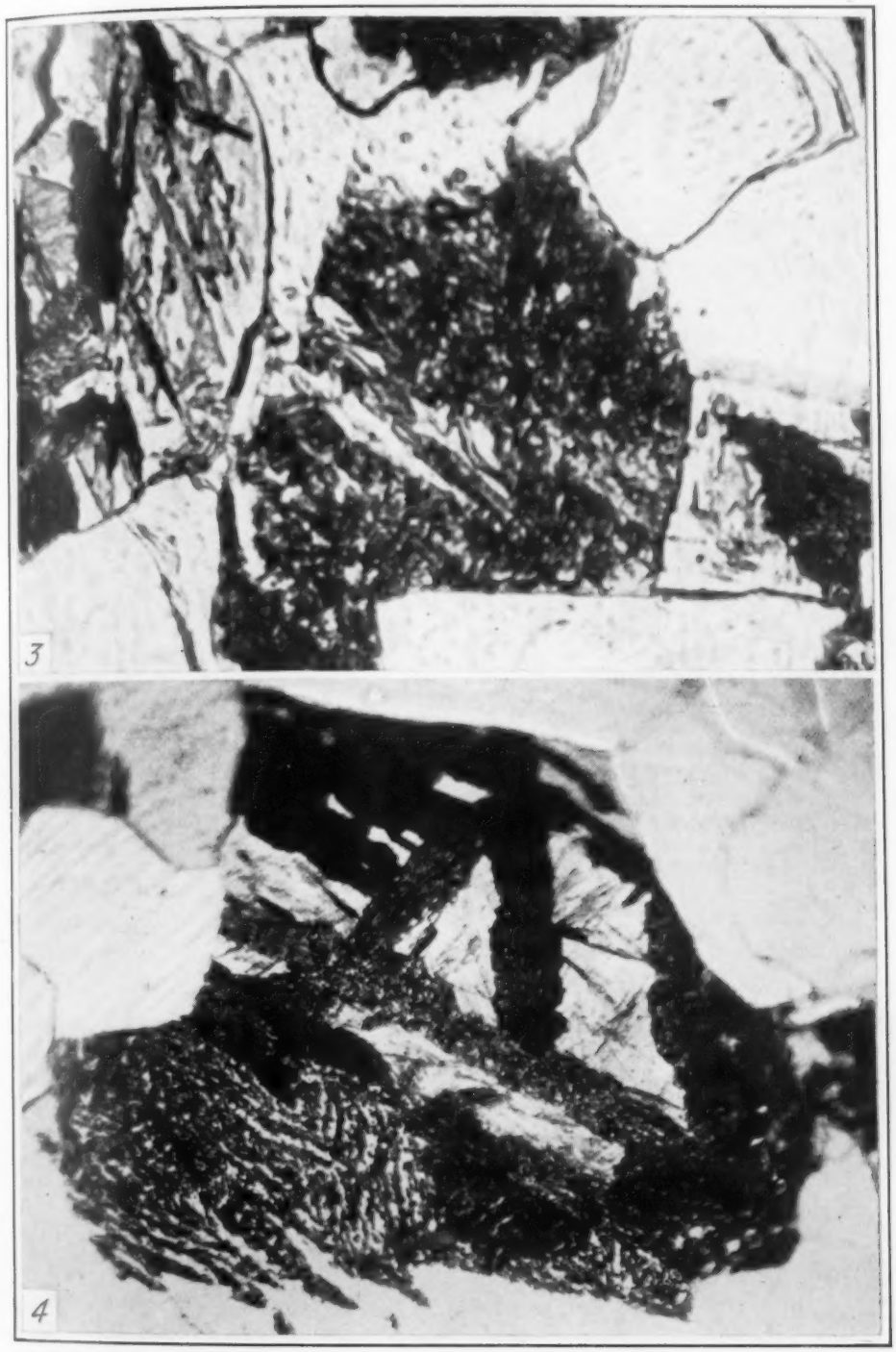


Fig. 3—Same as Fig. 2 but with Several Grains Partly Made Up of the Hardened Structure. × 2000.

Fig. 4—Same as Fig. 2 Showing One Large Grain of Pearlite with Islands of the Hardened Structure Completely Surrounded by Pearlite. × 2000.

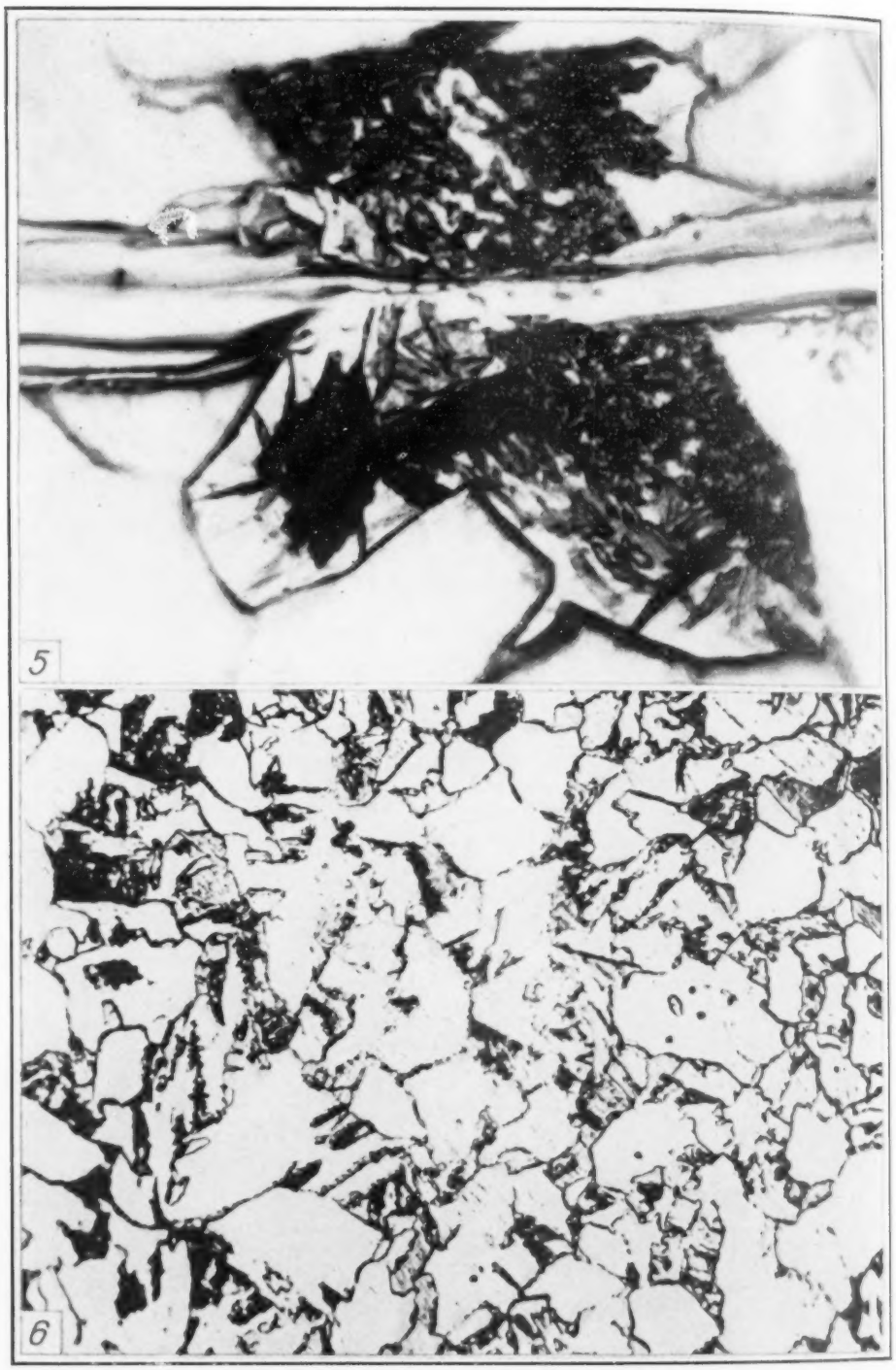


Fig. 5—Same Steel and Treatment as Figs. 1 to 4, with a Microcharacter Scratch Showing the Hardness of the Ferrite, Pearlite, and Austenito-Martensitic Structure. × 2000.

Fig. 6—S.A.E. 4615 Good Machining Steel Heated Two Hours at 1800 Degrees Fahr., Cooled in the Furnace to 1600 Degrees Fahr., and then Cooled in Still Air. Several Partially Martensitic Grains are Visible. × 1000.

show the different locations. Fig. 5 is that of a microcharacter scratch across a mixed grain showing the martensite to be much harder than the ferrite and also harder than the pearlitic portion of the same grain. The Brinell hardness was only 156.

The effect of cooling rate on the above heat of steel was similar to that on those described later. A sample carburized at 1700 degrees Fahr., for 15 hours and cooled in the box did not show any martensite. The grain size was No. 8 and the structure the usual one for S.A.E. 4615. Only small samples of this heat were available so that the effect of the structure on machinability could not be determined. The results from the microcharacter offer a probable explanation for the difficulties in machining. The presence of the hard particles cannot be detected by the Brinell test, since they are merely pushed into the softer ferritic matrix. The action might be compared to the Brinelling of gray cast iron containing excess carbide particles. There also, the Brinell hardness may not be a guide for machinability.

Experimental

The relationship between structure and machinability, that is, tool life and smoothness of finish, has been studied on other heats of S.A.E. 4615. This steel was of higher manganese content, made in the electric furnace and by a different steel company. Two heats were selected because of the known difference in their machining qualities after the preliminary treatment given them.

Machining Quality	C	Mn	P	S	Si	Ni	Mo	Grain Size
Poor	0.21	0.69	0.021	0.018	0.28	1.84	0.24	7-8
Good	0.15	0.65	0.022	0.032	0.26	1.80	0.23	6-8

The McQuaid-Ehn test showed the usual "moly" type of structure mostly number 8 in both, with a little more variation in the good cutting steel which also showed banding in both the case and the core. The normalizing treatments given these two heats were not identical. Various cooling cycles were therefore given to determine if the difference was in the steel or treatment. Samples were cut from machined parts and were necessarily irregular in shape, but were approximately one inch square by ¾ of an inch in thickness.

Table II gives the Brinell hardness obtained after the treatments listed in Table I. The apparent irregularity in the series 1-10

Table 1

Treatment No.	Treatment After Holding 2 Hours at 1800 Degrees Fahr.
1	Cool direct in air.
2	Cool in furnace to 1600 degrees Fahr., and then air cool.
3	Cool in furnace to 1400 degrees Fahr., and then air cool.
4	Cool in furnace to 1300 degrees Fahr., and then air cool.
5	Cool in furnace to 1200 degrees Fahr., and then air cool.
6	Cool in furnace to 1100 degrees Fahr., and then air cool.
7	Cool in furnace to 1000 degrees Fahr., and then air cool.
8	Cool in furnace to 900 degrees Fahr., and then air cool.
9	Cool in furnace to 800 degrees Fahr., and then air cool.
10	Cool in furnace till cold.
11	Transfer to furnace at 1200 degrees Fahr., hold 15 minutes, air cool.
12	Transfer to furnace at 1200 degrees Fahr., hold 1 hour, 15 minutes, air cool.
13	Transfer to furnace at 1200 degrees Fahr., hold 1 hour, 15 minutes, water quench.
14	Transfer to lead at 1200 degrees Fahr., hold 3 minutes, water quench.
15	Transfer to lead at 1200 degrees Fahr., hold 1 hour, water quench.
16	Transfer to lead at 1200 degrees Fahr., hold 3 minutes, air cool.
17	Transfer to lead at 1200 degrees Fahr., hold 1 hour, air cool.
18	Transfer to lead at 1200 degrees Fahr., hold 2 minutes, cool in furnace from 1200 degrees Fahr.
19	Transfer to lead at 1200 degrees Fahr., hold 1 hour, cool in furnace from 1200 degrees Fahr.
20	Transfer to furnace at 800 degrees Fahr., hold 15 minutes, air cool.
21	Transfer to furnace at 800 degrees Fahr., hold 1 hour, 15 min., air cool.
22	Transfer to furnace at 800 degrees Fahr., hold 1 hour, 15 min., water quench.

is probably due to the limited number of samples tested failing to give a good average. A difference was found between the two heats of steel, but it was a difference in degree rather than an entire difference in action. The steel which gave the difficulty in machining was harder through all the ranges of treatments probably due to higher carbon content. It showed greater air hardening with less ferrite separation when cooled from above the critical range and more martensite when cooled in air from within the critical range. Slow cooling to a slightly lower temperature also was required to eliminate all of the martensite. The difficulty in machining was probably largely due to the difference in treatment rather than the inherent difference in the steel. The structures described and photographs shown will therefore be mostly of the heat with good machining properties.

Figs. 6 to 10 show the structures obtained after heating to 1800 degrees Fahr., and cooling in the furnace to the temperatures mentioned and then cooled from those temperatures in still air. The direct air cool from 1800 degrees Fahr., is not shown since it was very similar to that cooled from 1600 degrees Fahr. As the critical range is entered, ferrite separation and banding occur with local increase in carbon concentration and the formation of more and larger martensitic grains. By cooling to 800 degrees Fahr., that is below Ar_1, martensite is no longer formed and little difference in

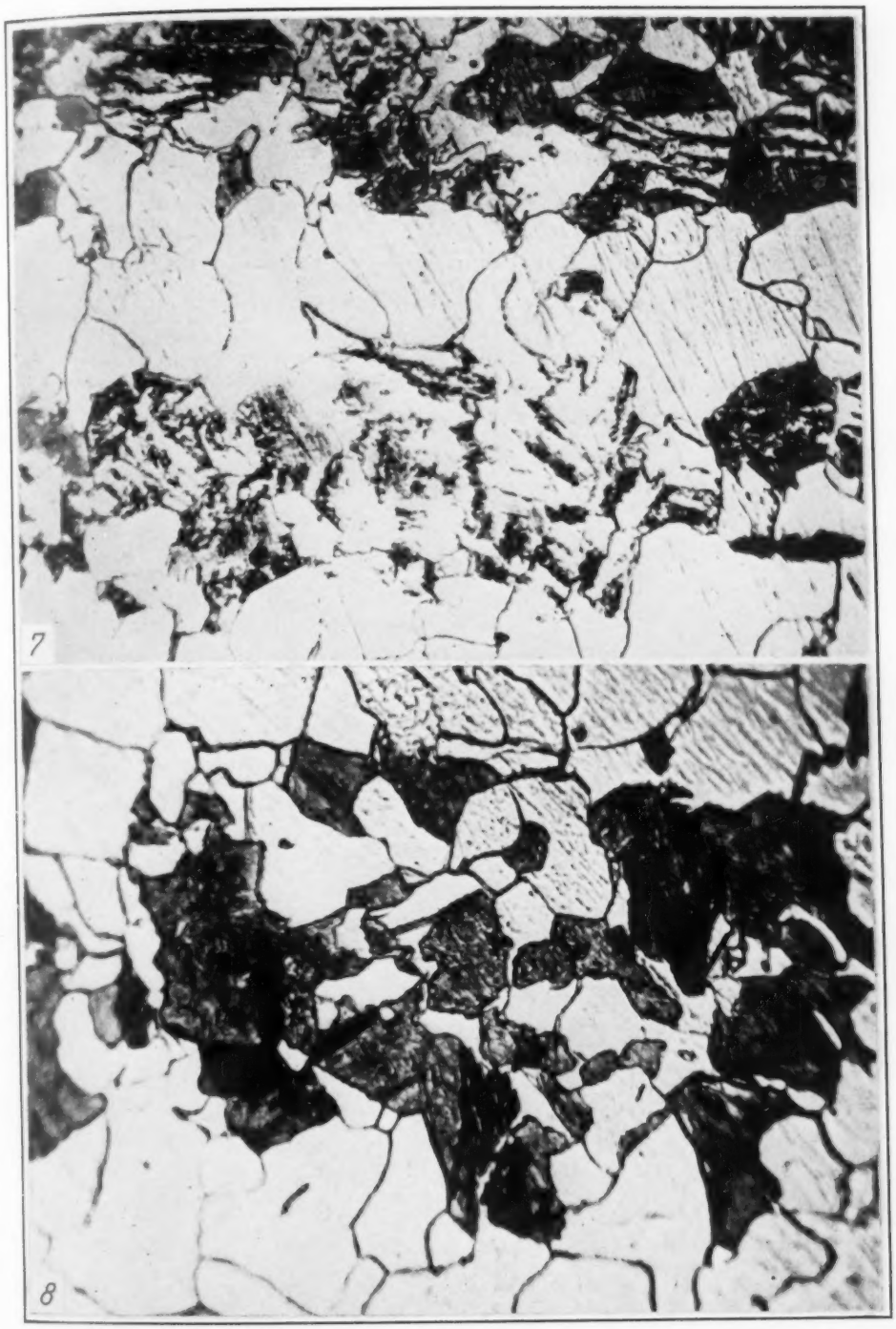


Fig. 7—Same as Fig. 6 but Air-Cooled from 1400 Degrees Fahr. Note Banding and Coarsening of Structure as well as Martensitic Formation. × 1000.

Fig. 8—Same as Fig. 6 but Air-Cooled from 1200 Degrees Fahr. Structure Banded and Still Coarser with More Martensite. × 1000.



Fig. 9—Same as Fig. 6 but Air-Cooled from 1000 Degrees Fahr. Structure Similar to Fig. 8. × 1000.

Fig. 10—Same as Fig. 6 but Air-Cooled from 800 Degrees Fahr., Grain Size and Banding Similar to Figs. 8 and 9, but Martensite has disappeared. Some of the Pearlite is Partially Spheroidized. × 1000.

Table II

Brinell Hardness Obtained After Heat Treatments Given in Table I

Treatment No.	Brinell Hardness	
	Good Cutting Steel	Poor Cutting Steel
1	174	207
2	174	207
3	183	217
4	179	202
5	192	202
6	179	207
7	163	212
8	159	179
9	146	156
10	149	159
11	166	187
12	187	202
13	...	235
14	217	...
15	163	...
16	170	...
17	156	...
18	149	...
19	156	...
20	163	192
21	163	187
22	170	209

structure results below this temperature, even when furnace-cooled to room temperature. Banding develops during slow cooling in steel which has the tendency to do so.

In an attempt to eliminate the banding by faster cooling and perhaps some of the martensite also, because of more even carbon distribution, samples were transferred from 1800 degrees Fahr. to a furnace set at 1200 degrees Fahr. Some were held for 15 minutes or merely long enough to allow the sample to reach 1200 degrees Fahr., and others for one hour longer. These samples did show less banding but also showed considerable ferrite separation and martensitic formation. The unexpected result was the formation of much more martensite when held for the longer time at 1200 degrees Fahr. The grain is also somewhat coarser. Figs. 11 and 12 show these structures. Fig. 13 is taken from a sample quenched in water after being held at 1200 degrees Fahr., for 15 minutes, indicating that the pearlite in the others formed during air cooling below 1200 degrees Fahr. This last sample, however, was taken from the poor machining heat. Still more rapid cooling from 1800 to 1200 degrees Fahr., was obtained by quenching the samples in molten lead at 1200 degrees Fahr., and further cooling as described in treatments 14 to 19 inclusive. Some of the structures are shown in Figs. 14 to 17. The lack of pearlite in Fig. 14 may have resulted from too short a time at 1200 degrees Fahr., before quenching, since the longer

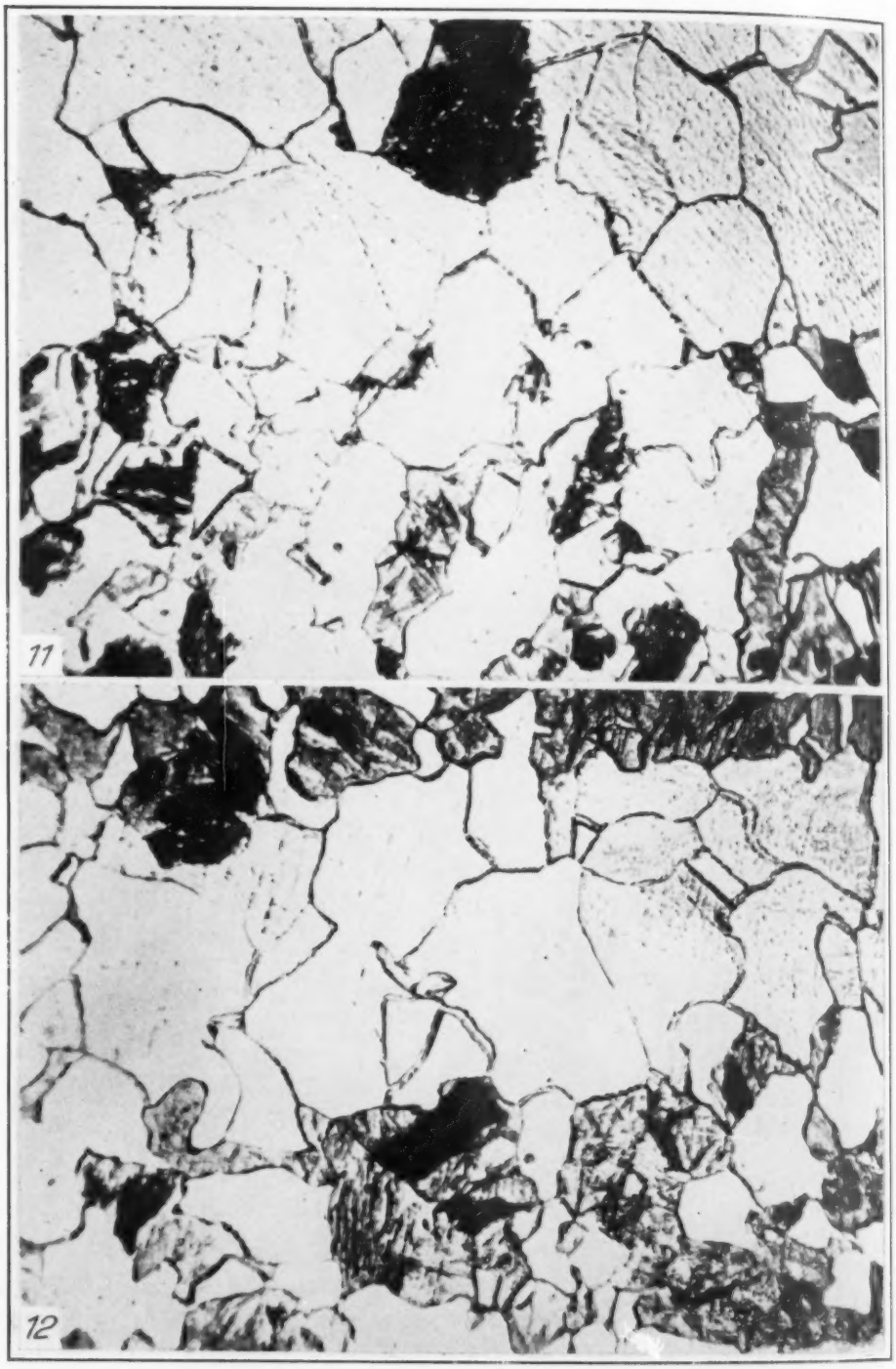


Fig. 11—S.A.E. 4615 Given Treatment No. 11, Table I. The More Rapid Cooling Through the Upper Critical Range has Suppressed Banding. Martensitic Grains are Present. × 1000.

Fig. 12—Same as Fig. 11, Given Treatment No. 12. The Longer Holding at 1200 Degrees Fahr. Before Air Cooling has Resulted in the Formation of More Martensite and More Pronounced Banding. × 1000.

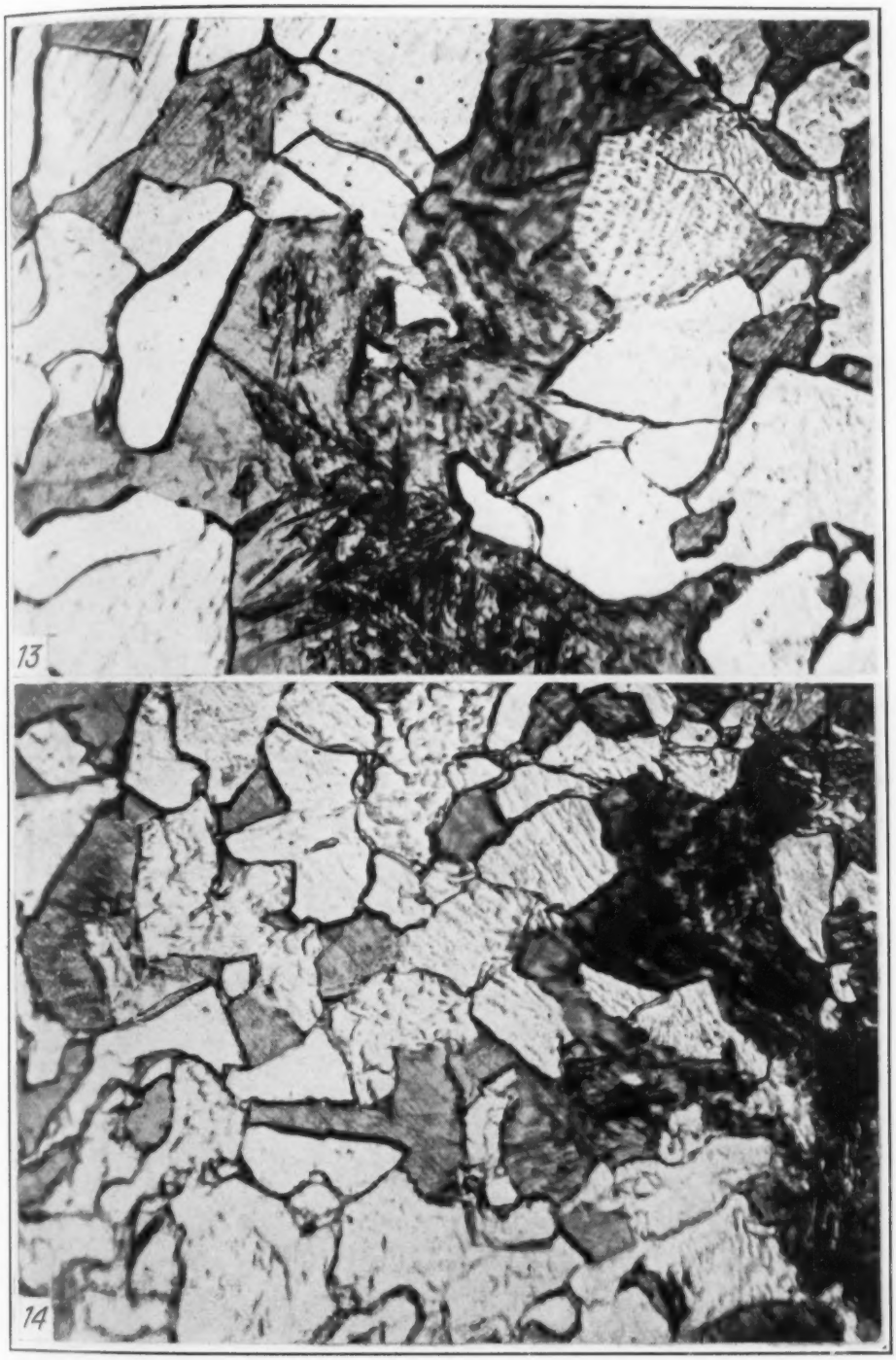


Fig. 13—S.A.E. 4615, Poor Machining Heat, Given Treatment No. 13. The Water Quench from 1200 Degrees Fahr. has Held the Carbon Almost Entirely in the Martensitic Structure. × 1000.

Fig. 14—S.A.E. 4615, Good Machining Heat, Given Treatment No. 14 Table III. Water Quenching from 1200 Degrees Fahr., has Again Produced Martensite and Pearlite. The darkened grains at the right are the result of faulty illumination. They are martensitic also.) × 1000.

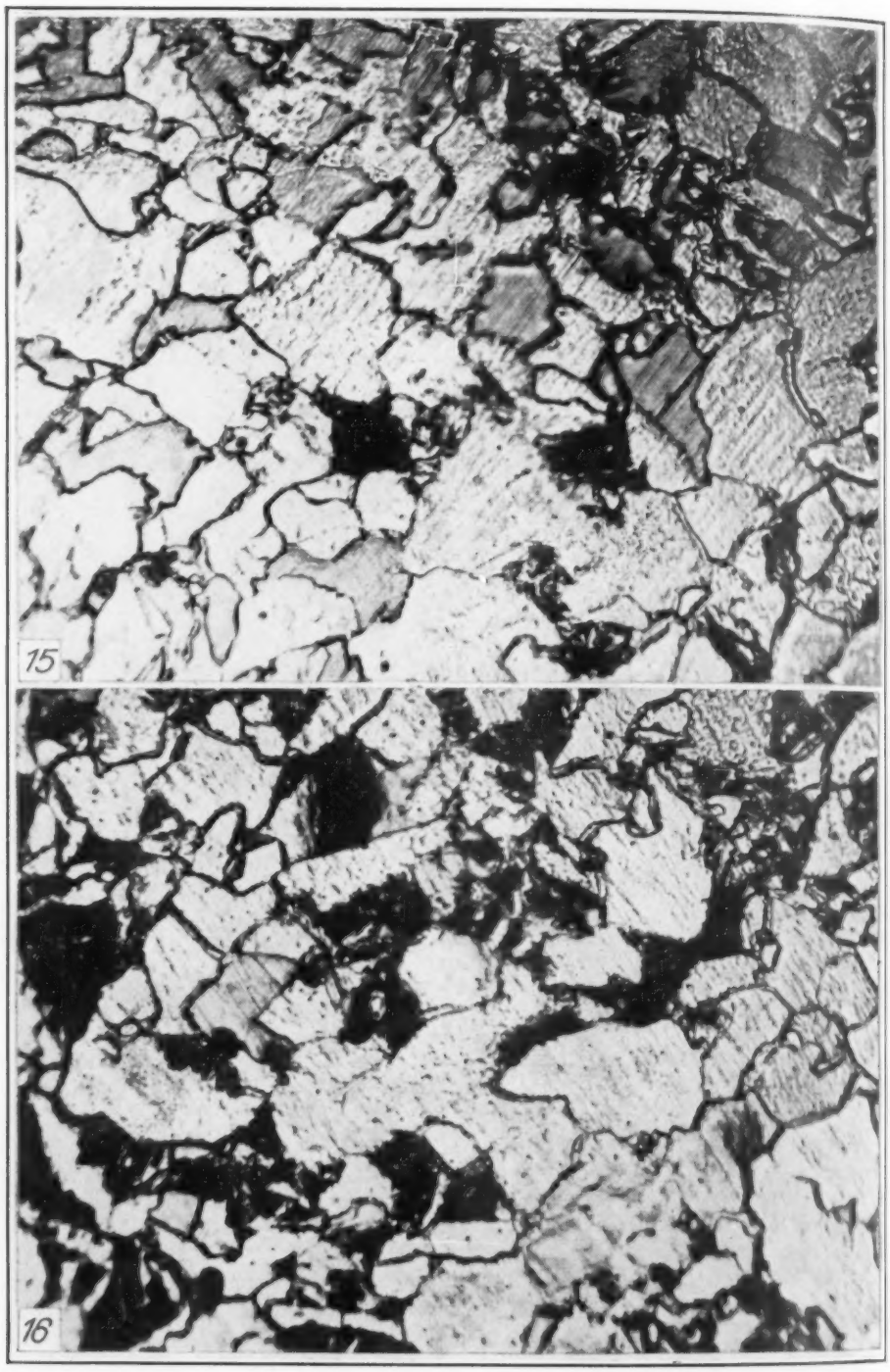
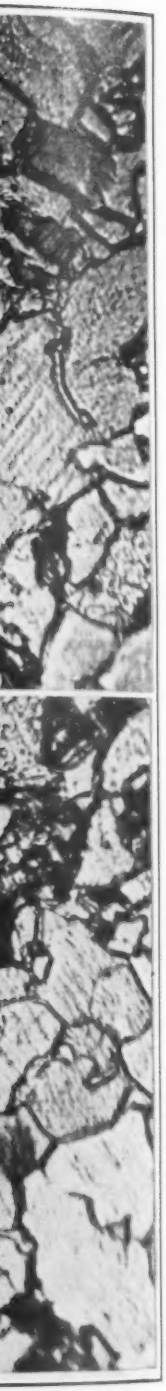


Fig. 15—Same Steel as in Fig. 14, Given Treatment No. 15. Longer Holding at 1200 Degrees Fahr., Before Water Quenching has Resulted in the Formation of Some Pearlite. The Rapid Cooling Through the Upper Critical Range has Eliminated Banding but Still Permitted Ferrite Separation. × 1000.

Fig. 16—Same as Fig. 14, but Given Treatment No. 16. The Air Cool Instead of a Water Quench from 1200 Degrees has Produced More Pearlite but Several Martensitic Crystals are Still Visible. × 1000.



Longer Holding at
Formation of Some
Eliminated Banding

ir Cool Instead of
Several Martensitic

time in this case shows some pearlite. Even this more rapid cooling rate given these samples allows considerable ferrite separation, which is probably necessary to easy machining because of the coarsening of the structure produced thereby. On the other hand, too slow cooling will produce banding and separation of ferrite into large areas which are believed to give poor finish. The results here obtained show banding to take place during slow cooling in the upper part of the critical range, but a more rapid rate of cooling if carried through the lower part of the critical range will produce martensitic crystals detrimental to tool life and finish.

Banding Eliminated

To accomplish the desired results, treatments 20 to 22 were given. By transferring the samples from a furnace at 1800 degrees Fahr. to one at 800 degrees Fahr., the rate of cooling would automatically become slower as 800 degrees Fahr. was approached. Figs. 18 to 20 show the uniformity of the structures obtained; although 800 degrees Fahr. is apparently a little too high if the samples are not held long enough at this temperature or if they are water quenched. This was more pronounced in the heat of steel that machined poorly. It is believed that the structure produced will approach the ease of machinability and cutter life obtained with furnace cooled material, but will still retain sufficient uniformity of structure to give a good finish. This was checked on production parts by a similar treatment except that the lower furnace was about 600 degrees Fahr. before placing the heated parts in it. The heat from several hundred pounds of metal raised the temperature to about 1050 degrees Fahr. This dropped back 100 to 200 degrees Fahr. in a short time and then more slowly till below 800 degrees Fahr. The parts so treated were taken from a lot giving trouble, since only eight or ten pieces per cutter grind were being produced. After the above treatment, the entire lot of 100 pieces were machined without grinding the cutter and a much better finish obtained. Repeated checks have given similar results.

Present Commercial Normalizing Cycles Not Regulated to Produce Best Results

The usual commercial practice in normalizing this type of steel

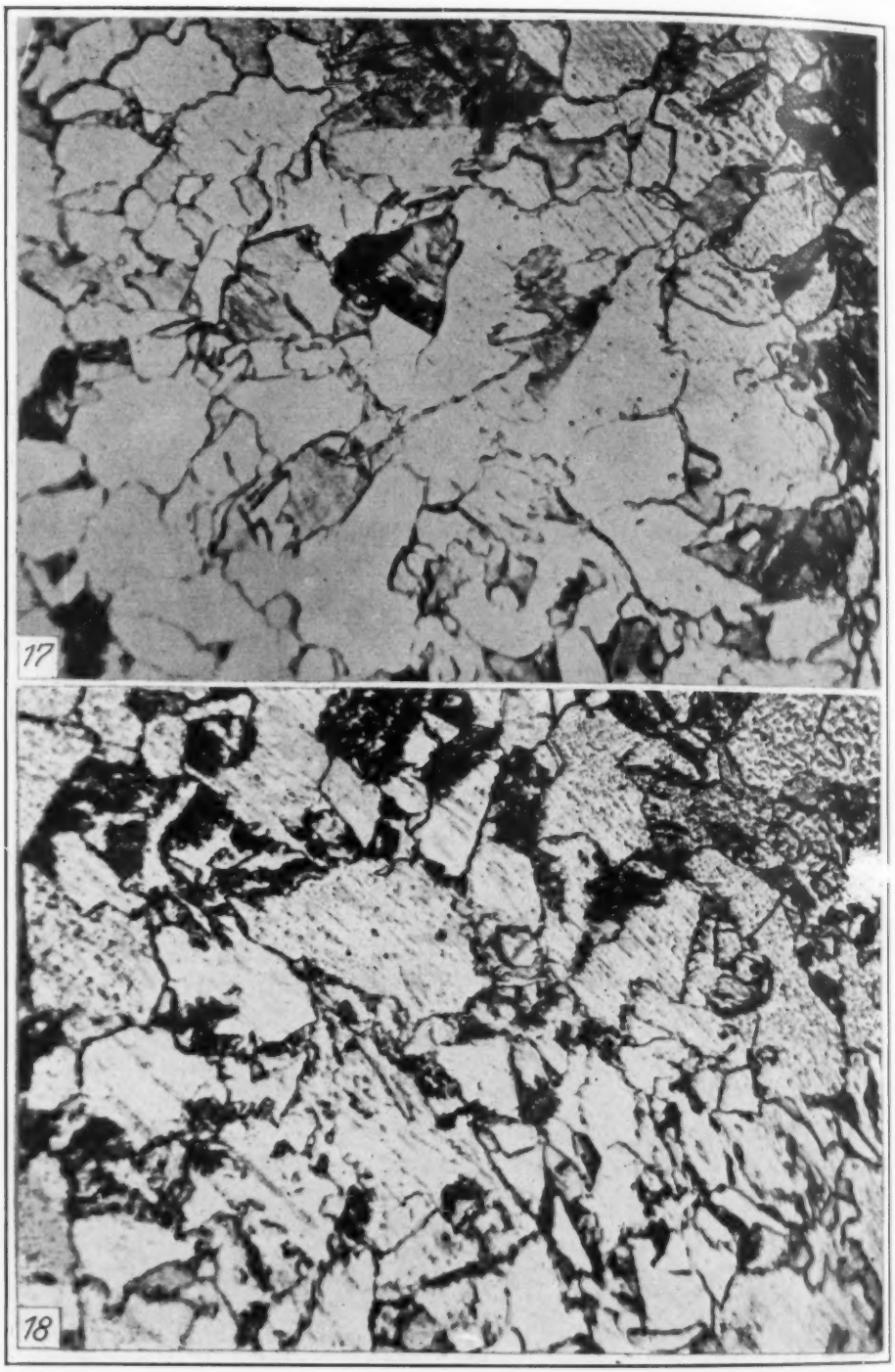


Fig. 17—Same Treatment as Fig. 16, but Held One Hour Longer at 1200 Degrees Fahr., Before Air Cooling. The Longer Time at 1200 Degrees Fahr., has Again Resulted in the Formation of More Martensite Just as It Did in Fig. 12. × 1000.

Fig. 18—S.A.E. 4615, Good Machining Heat, Given Treatment No. 20. The Structure Showed a Slight Pattern with Coarser and Finer Areas. Some Martensite is Evident in the Fine Areas Indicating that 800 Degrees Fahr. is a Little too High or the Time of Holding was not Long Enough. × 1000.

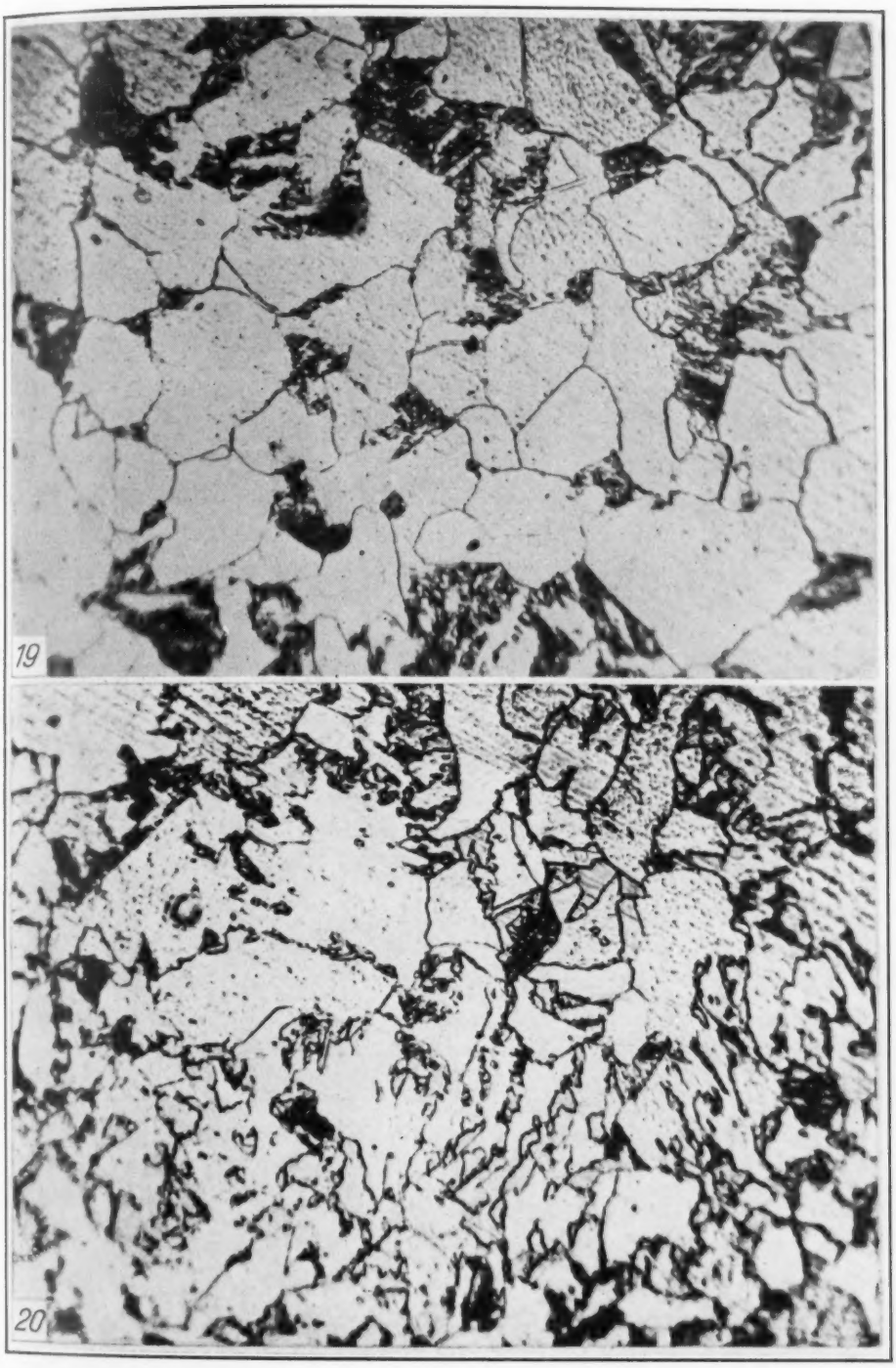
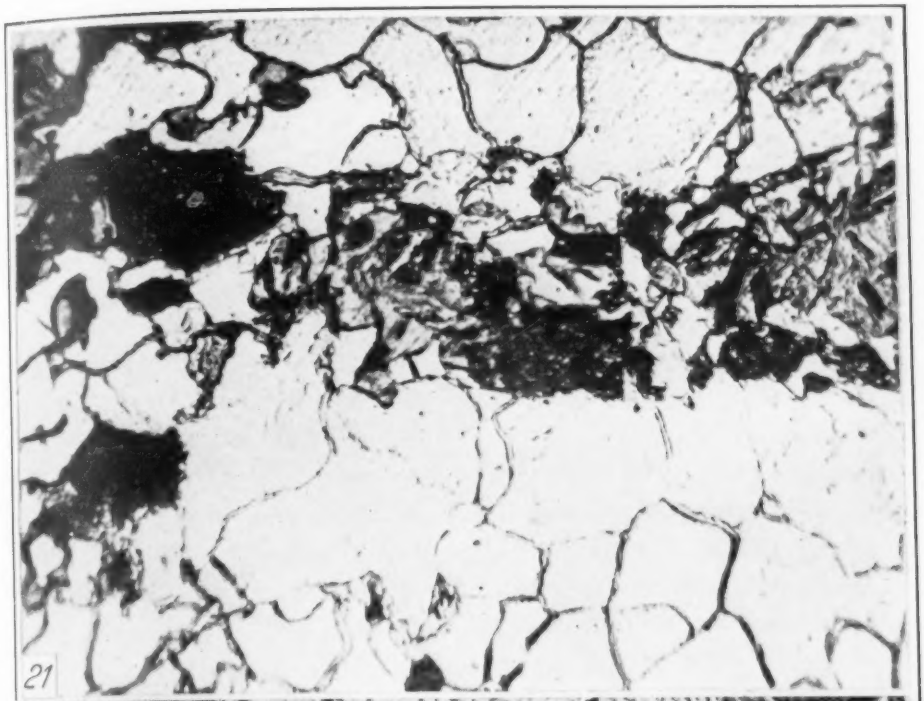


Fig. 19—Same as Fig. 18, Given Treatment No. 21. Faster Cooling Through the Upper Critical Range has Practically Prevented Banding and Slow Cooling Through the Lower Range Has Eliminated Martensite. × 1000.

Fig. 20—Same Treatment as in Fig. 19, but Water-Quenched from 800 Degrees Fahr., Instead of Air Cooling. This Sample Shows a Pattern Effect with Martensite in the Finer Grains Indicating that 800 Degrees Fahr. is not Quite Low Enough for the Lower Limit of Slow Cooling if Followed by a Water Quench. × 1000.

is either to heat the parts in a batch type furnace at 1650 to 1800 degrees Fahr., and pull out into air or else to run them through a continuous furnace whose maximum temperature is the same as in the batch type and with a temperature of 1200 to 1000 degrees Fahr. or at least above Ar_1, at the discharge end.

The use of high temperatures of 1800 degrees Fahr. or above in normalizing is to develop coarse-grained pearlite which is usually conceded to be the most desirable structure for machining in the types of steel experimented with. Furnace cooling from these temperatures consumes too much furnace time and adds to the cost. Direct air cooling from the batch type furnace produces a uniform finer grained structure relatively free from banding and gives a good finish in machining, but tool life and ease of machinability are not as good as with softer structures. For heats subject to such formations, the continuous cycle promotes banding by slow cooling in the furnace at high temperatures and more rapid cooling through Ar_1 to form martensite. The heat designated as poor machining, had been put through a continuous counterflow furnace and discharged at about 1000 degrees Fahr. This furnace was of the latest type electrically heated with the work passing through single file travelling in opposite directions, one row entering from each end of the furnace. Cooling in the lower critical range was therefore accelerated by cold work entering in the adjacent row. The good machining sample had been normalized in an oil-fired straight through pusher furnace whose discharge end temperature was approximately 800 degrees Fahr. The work from the counterflow furnace was banded and contained considerable martensite in some of the pearlite bands, while other bands were nearly free from that constituent. The work from the straight through furnace contained no martensite. When a sample of the poor machining steel was normalized in the straight through furnace, it contained but few hard grains. As the poor machining parts had all been semi-machined before reaching the finish machining operation, they could not be re-run through the high temperature cycle. In place of this they were given a draw at 1200 degrees Fahr., for two hours. The Brinell hardness was only slightly reduced but the cutter life increased from three or four pieces per grind, all of rather poor finish, to 35 or 40 pieces per grind and at the same time the surface finish was greatly improved. The expected tempered structure was produced in the former martensitic grains.



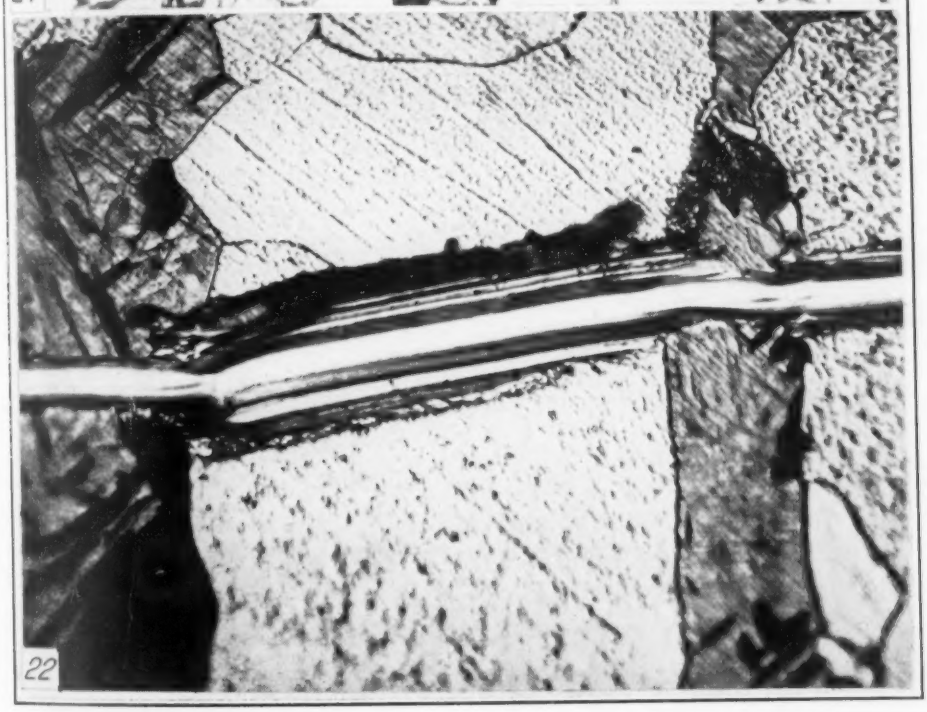


Fig. 21—S.A.E. 4615, Good Machining Heat, Held Two Hours at 1600 Degrees Fahr., Cooled in the Furnace to 1000 Degrees Fahr., and Then Air-Cooled. The Structure Consists of Bands of Ferrite and Mixed Pearlite and Martensite. Maximum Temperature of Heating is Therefore not the Governing Factor in the Formation of Martensite. × 1000.

Fig. 22—Coarse-Grained S.A.E. 4615, Heated to 1800 Degrees Fahr., Furnace-Cooled to 1200 Degrees Fahr., and then Air-Cooled. The Microcharacter Scratch Shows the Hardness of the Martensitic Grains. × 1000.

An attempt was made to machine parts which had been drawn at 1200 to 1300 degrees Fahr., after cooling from the forge hammer. The cooling rate from the high temperature had been too rapid and a Widmanstatten structure with but little ferrite granulation had resulted, the structure approaching more nearly to that of a quenched and drawn part. Machinability was poor. It is possible that good results might be obtained by placing forgings directly from the hammer in a furnace held at 600 to 800 degrees Fahr. to obtain the proper cooling cycle.

Samples were also cooled in the furnace from 1600 to 1200 degrees Fahr., and 1000 degrees Fahr., followed by an air cool to determine the effect of maximum temperature on the martensitic formation. The structure was somewhat finer grained and contained a little less martensite, but it was still present in considerable quantities as shown in Fig. 21. Holding for one hour at 1000 degrees Fahr. had little effect on the structure. Lower normalizing temperatures would not be commercially desirable and no lower temperatures were used.

The two heats experimented with above, were of recent manufacture with higher manganese content than formerly used. Two heats of steel made about three years ago with the old manganese limits, one fine, one coarse-grained were heated to 1800 degrees Fahr., furnace cooled to 1200 and 1000 degrees Fahr., and then air cooled. Both contained martensite. The structure of the coarse-grained heat is shown in Fig. 22, with a microcharacter scratch again showing the hardness of the martensitic grains.

	C	Mn	P	S	Si	Ni	Mo	Grain Size
Fine	0.17	0.54	0.017	0.020	0.29	1.77	0.25	7-8
Coarse	0.16	0.54	0.030	0.020	0.11	1.82	0.24	3

Not Produced in All Steels

Experiments were made on other types of steel to determine if the structure was peculiar to nickel-molybdenum steel. Table III shows types of steel and treatments given after being held at 1800 degrees Fahr., for about two hours, cooled in the furnace to the temperature given in the table, and air-cooled from that temperature.

S.A.E. 2512 after cooling in air, produced the structure shown in Fig. 23, containing a large amount of martensite. A sample

Table III
Treatments Given After Holding 2 Hours at 1800 Degrees Fahr.

Steel	Brinell	Furnace Cool to Degrees Fahr.	Structure
2512	179	1000	Ferrite and martensite, some pearlite.
2512*	174	800	Ferrite and pearlite, some martensite.
2315	183	1300	Mostly Widmanstatten structure. Some martensitic indication.
2315	149	1100	Ferrite, pearlite with traces of martensite.
2315*	134	900	Ferrite, pearlite. No martensite.
3115	179	1400	Ferrite, pearlite, some Widmanstatten structure.
3115	153	1200	Ferrite, pearlite. No martensite.
3115*	156	1000	Ferrite, pearlite. No martensite.
3½% Ni, Mo.	223	1100	Ferrite and Widmanstatten structure. Traces of martensite.
	235	900	Mostly ferrite and martensite.
6115	217	1400	Ferrite, pearlite. No martensite.
6115	149	1200	Ferrite, pearlite. No martensite.

*Not the same heat of steel as the others of that type.

cooled to 800 degrees Fahr. consisted mostly of pearlite and ferrite.

Some partially martensitic appearing grains developed in S.A.E. 2315 after cooling from 1300 and 1100 degrees Fahr., but no pronounced martensitic structures were produced.

The structure did not develop in either 3115 or 6115, the latter being shown in Fig. 24 after cooling in air from 1200 degrees Fahr.

The 3.5 per cent nickel-molybdenum steels after cooling from 1100 degrees Fahr., gave the pronounced Widmanstatten structure of Fig. 25, with a few grains of martensite and with ferrite banding. When cooled in air from 900 degrees Fahr., it consists mostly of ferrite and martensite, as in Fig. 26. It may be possible that the finer particles of Fig. 25 are also martensite, but not sufficiently resolved by the objective to be recognized as such. A limited number of samples of these latter types were tested, but they do show that the martensitic structure is much less apt to occur in some steels than in others.

Theoretical Considerations

The cause of the martensitic formation has not been determined. A possible explanation is the segregation of the alloying elements in the steel. It is, however, rather difficult to think that segregation would cause small grains of martensite to be uniformly distributed throughout the sample when cooled from a high temperature, and coarse grains in a banded formation when air-cooled from just above Ar_1. Andrew and Dickie[1] state that in the Ar_1 range, the

[1] "Ac_1 Range in Special Steels," *Journal*, Iron and Steel Institute, No. 1, 1927.

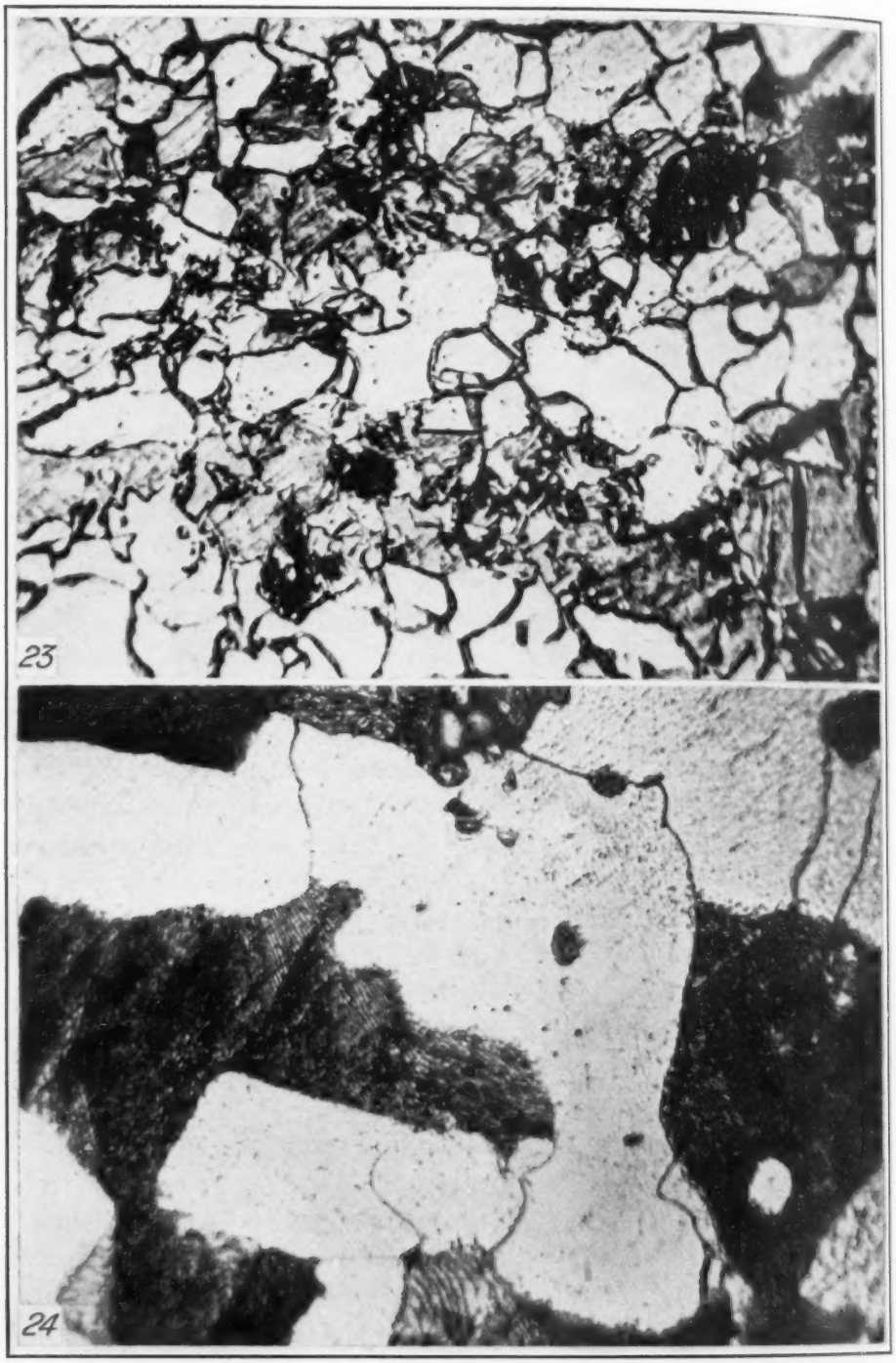


Fig. 23—S.A.E. 2512, Treated as in Table III and Air-Cooled from 1000 Degrees Fahr. Not Much of the Austenite has Transformed to Pearlite. × 1000.

Fig. 24—S.A.E. 6115, as Treated in Table III and Air-Cooled from 1200 Degrees Fahr. The Structure Consists of Ferrite and Fine Lamellar Pearlite. No Martensite was Formed. × 1000.

Analysis:—C, 0.19, Mn, 0.76, P, 0.019, S, 0.034, Si, 0.19, Cr, 0.89, V, 0.18 Per Cent. Grain Size No. 8.



Figs. 25 and 26—A 3.5 Per Cent Nickel-Molybdenum Steel Heated to 1800 Degrees Fahr., Cooled in the Furnace to 1100 and 900 Degrees Fahr., Respectively, and then Air-Cooled. These Structures Show that more Martensite is Formed by Air Cooling if the Steel has First Been Slowly Cooled to Nearly Ar_1, to Permit Ferrite Separation and Localized Carbon Concentration. × 1000.

pearlite first separating will have higher carbide content and lower nickel than obtained on an average after the pearlite is formed. Whitely[2] mentions phosphorus diffusion and adds that other elements may be redistributed also. Hallimond[3] and Whitely[4] mention the effect of supersaturation in producing areas of different hardenability. Jones[5] states that the hardenability may also be influenced by the manganese content if nickel is segregated. Kjerrman[6] describes the effect of different elements in causing the pearlite transformation to take place over a range of temperature, but states that long annealing and slow cooling promotes homogeneity more than normalizing through the range. The present investigation has shown that slow cooling during the upper part of the critical range promoted banding and the subsequent formation of martensite. Hultgren[7] states that on heating, the austenite formed in the Ac_1 transformation is heterogeneous, conforming closely to the pre-existing pearlite. It might be assumed that the reverse takes place on cooling but it does not explain why different grains or parts of the same grain should produce martensite or martensite and austenite while the remainder produce pearlite at the same rate of cooling.

The separation of ferrite and concentration of carbon into grains approaching eutectoid composition during slow cooling in the upper critical range is believed to be the explanation for the greater amount of martensite formed on subsequent air cooling than when directly air-cooled from high temperatures which prohibits carbon concentration. The variation from grain to grain and from one part of a grain to another is probably caused by segregation of elements and supercooling. Air cooling is just fast enough to prevent the transformation in some areas and not in others.

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[2] "The Ac_1 Range in Alloy Steels," *Journal*, Iron and Steel Institute, No. 1, 1927.

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[3] "On Delayed Crystallization in the Carbon Steels; The Formation of Pearlite, Troostite and Martensite," *Journal*, Iron and Steel Institute, No. 1, 1922.

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[4] "On the Diminution of Lag at Ar_1 Through Deformation," *Journal*, Iron and Steel Institute, No. 2, 1922.

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[5] "The Properties of Nickel Steels with Special Reference to the Influence of Manganese," *Journal*, Iron and Steel Institute, No. 1, 1928.

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[6] "The Effect of Manganese, Silicon and Phosphorus on the Pearlite Interval," B. Kjerrman, TRANSACTIONS, American Society for Steel Treating, March, 1926.

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[7] "The Ac_1 Range of Carbon Steel and Related Phenomena," Axel Hultgren, TRANSACTIONS, American Society for Steel Treating, August, 1929.

Summary and Conclusion

The results of this investigation have shown that:

1. Martensite or martensite in an austenitic matrix may occur in air-cooled low carbon steels in certain alloy steels of fairly low alloy content.

2. Slow cooling (such as furnace cooling) above the Ar_1 point, followed by an air cool through Ar_1, produces more martensite than a direct air cool from a higher temperature. The slower cooling permits ferrite separation and higher local carbon concentration and perhaps some segregation of alloying elements as well.

3. With faster cooling to a point above Ar_1, holding at this point and then air cooling through Ar_1, those samples held longer contained much more martensite than those air-cooled as soon as temperature equilibrium had been reached. This was an unexpected result, and no explanation was found. The longer holding time may have permitted more segregation.

4. Banding was found to develop during slow cooling in the upper part of the critical range, but did not occur to any extent in the lower part of the range if cooled more rapidly through the upper critical range.

5. A combination treatment was arrived at giving relatively fast cooling in the upper critical range to eliminate banding and slow cooling through Ar_1, to eliminate the formation of martensite. This was accomplished by transferring the metal from a furnace at the high normalizing heat, to one near the Ar_1 point (or below it if the parts contain sufficient heat to raise the furnace temperature above Ar_1), cooling through Ar_1 in the furnace, and then followed by any desired rate of cooling. It is believed a satisfactory cycle can be obtained in a continuous type furnace. Transferring parts direct from the forge hammer to a furnace at the low temperature only might produce a satisfactory structure, but this has not been tried.

6. Treatments as in paragraph five are suggested for tool life and surface finish in subsequent machining and are not claimed to permanently eliminate banding. No checks were made after a subsequent heating. The structure produced was expected to approach the ease of machinability of fully annealed steel, but still eliminate the soft ferrite bands and provide the uniformity necessary for good finish as might be expected from quenched and drawn material.

The actual results in production confirmed this by showing a remarkable increase in number of pieces per grind of cutters and at the same time a better finish on machined parts.

7. The presence of the martensitic grains cannot be detected by Brinell hardness checks, as but little increase was shown with increase of martensite. The ball impression is much too large, the hard grains merely being pressed into the soft ferritic matrix. The microcharacter scratch does show the greater hardness of the martensite and its probable effect on tools.

8. A few tests on different types of steel show that martensite does not always form. The number of tests was not sufficient to say definitely that one type of steel was more susceptible than others, but it could be produced in all the nickel-molybdenum steel tested. Some steels with greater hardening power when water or oil-quenched from above the critical range, did not produce martensite on air cooling while others with less hardening power contained much martensite after air cooling. Further investigation is needed to determine the cause of the martensitic formation.

Acknowledgments

The author wishes to acknowledge the help of valuable suggestions from H. W. McQuaid, chief metallurgist of the Timken-Detroit Axle Co., and is indebted to Roy Roush of the Cadillac Motor Car Co. for the photomicrographs.

DISCUSSION

E. E. Thum:[1] I think Mr. McMullan's paper describes something which might be termed a "disease"; fortunately he has found a remedy. The next step appears to be to pursue the inquiry (and this is probably a job for the steel makers) and discover what the essential cause of the disease is and remove that cause. When that is accomplished the rather complicated heat treatment which is necessary to cure defective material can be abandoned for a simpler operation.

The micrographs shown very clearly indicate the presence of martensite alongside of well-decomposed areas which at one time were martensite. These micros, I understand, were taken from a low nickel steel. I wonder if this is not an indirect indication that nickel itself is segregated in the steels. To support this suggestion is the well known fact that nickel has a powerful effect on depressing the transformation point. The only thing which suggests itself to my mind as a reason for the close proximity of two patches of material in

[1]Editor, *Metal Progress*, Cleveland.

such different metallographic conditions, is that one has a high alloy content, whereas the other has not.

This, however, violates another commonly-understood idea that nickel is quite soluble in ferrite. An iron-nickel alloy containing far more nickel than existed in these particular gear steels, would form a reasonably uniform solid solution after soaking above the critical temperature. Furthermore, the long heat treatment which Mr. McMullan finds to be incapable of removing the trouble, would rather cause the *diffusion* of nickel throughout the ferrite than cause its further segregation.

Perhaps the whole trouble is hooked up with something connected with the original banding of the steel; that is, some effect of the ingot segregation of unknown elements which cause the appearance of pearlite in well marked strips throughout rolled material. Or we may have to go even further back into the steel making and discover whether electric steel and its higher furnace and casting temperatures is somehow to blame.

At any rate, it seems to me that the study of the essential reason for the appearance of this duplex structure (certainly one not to be expected as an equilibrium structure) would be well worth while to remove the trouble of occasional hard spots from commercial metal.

O. W. Boston:[2] Mr. McMullan's paper is extremely interesting and gives valuable information relating to the structure and the resultant machinability of the work. As stated by Mr. McMullan, this work was necessitated by practical production trouble and was not carried on in the manner of a research project.

It is noted that, by good machinability, reference is made to good finish, long tool life, and ease of machining, all grouped together. It would be interesting if Mr. McMullan could differentiate between these three factors of machinability and give us further information as to the best structure for finish, for tool life, and for low power, as these three are believed to be quite independent factors.

Author's Closure

In regard to the segregation of nickel producing this structure, suggested as a possibility by Mr. Thum, as shown by photographs, the sample cooled directly in air from 1600 degrees Fahr. (that is above the critical range) produced a uniform fine-grained structure in which there were a number of small grains containing martensite. The same steel, taken from the same gear, when allowed to cool down to 1200 or perhaps 1000 degrees Fahr., produced martensitic grains in band formation. They were much larger, and there were of course fewer of them because the number of grains was much less.

It seems rather difficult to lay the blame entirely to segregation, requiring that segregated areas could, in this very short time, concentrate themselves from a large number of small grains to a fewer number of large grains. Also, as far as nickel itself is concerned, it happens with those particular heats of steel of S.A.E. 2315 with which I experimented, very little martensite was

[2]Director, Department of Engineering Shops, University of Michigan, Ann Arbor, Michigan.

found. Whether it just happens that something about the steel making process of those particular heats prevented this martensitic formation in them, I could not say. I do not believe it can be entirely a question of nickel segregation.

In reply to Professor Boston's discussion I do not believe, as Professor Boston has suggested, that tool life, low power, and surface finish are independent factors. In fact I believe they are quite dependent upon each other, even more or less in the relation of cause and effect from a commercial viewpoint at least.

If the steel being cut requires high power input, it means that the force on the tool must be that much greater, with consequently more wear on the cutting tool, more of a tendency to overheat and burn edges, and general deterioration of the tool. Tool life would, therefore, be greatly dependent upon the power necessary to cut the steel.

For quality of surface finish I believe that, if commercial considerations are neglected such as the time necessary to finish a certain article, the structure giving the best surface would be one as fine-grained and as uniform as possible. With such a structure, if the speeds, feed, depth of cut, etc., were reduced, a very good finish should be obtained because of the uniformity of the material, and the chip cut at all times should be very nearly the same. Such a structure would be obtaind in a hypoeutectoid steel by forming sorbite. With an eutectoid steel, a sorbitic structure also should be satisfactory, but a fine-grained pearlite would be quite similar since there is no excess constituent present. A spheroidized or partially spheroidized structure should also approach the two previous ones mentioned.

When the time factor for economic considerations enters, it is necessary to have the steel in a condition showing the lowest impact and hardness. In other words, the steel having the best machining properties would be one which has been referred to as a soft brittle steel. This condition would give long tool life because of the low power necessary, and at the same time give a reasonably good commercial finish. I am, of course, neglecting to consider the presence of hard abrasive nonmetallic material which might wear or nick the cutter. These, however, should not be present in a steel of good quality. The truth of these factors is shown by the ease of machinability of high sulphur screw stock compared to a steel of similar carbon content but with low sulphur which has high impact.

The structure which has given the best all around results in machining has been found to be a coarse-grained pearlite. This occurs naturally at the ordinary normalizing temperatures in coarse-grained steels, and is obtained in fine-grained steels by high normalizing temperatures. The coarse-grained structure gives the lower impact necessary for low power and long tool life, and at the same time a satisfactory finish with high cutting speeds necessary in commercial work.

THERMAL CONDUCTIVITY OF IRONS AND STEELS AND SOME OTHER METALS IN THE TEMPERATURE RANGE 0 TO 600 DEGREES CENT.

By S. M. Shelton and W. H. Swanger

Abstract

The thermal conductivities in watts cm^{-1} deg^{-1} have been determined over temperature ranges between 0 and 600 degrees Cent. for zinc, nickel, a few nickel alloys and twenty irons and steels selected as typical examples of commercial materials used for a variety of purposes. The method and apparatus are described. A comparative method of measurement was used, all values being referred to the thermal conductivity of lead, assumed to be 0.352 watts cm^{-1} deg^{-1} at 0 degree Cent.

For the pure metals and the irons and low alloy steels the thermal conductivities decrease with increase in temperature. The conductivities of the high alloy steels and of the nickel alloys increase with increase in temperature. In general, the thermal conductivities of all the materials tested are linear functions of the temperature within the range within which measurements were made. A noteworthy exception is nickel, for which a sharp change from a negative to a positive temperature coefficient of thermal conductivity occurs at the temperature of the magnetic transformation.

For the ferrous alloys, an increase in the amount of alloying constituents in iron causes, in general, an increase in the temperature coefficient of thermal conductivity. However, the many, and sometimes conflicting, factors concerned make it practically impossible to generalize concerning the quantitative relationship of thermal conductivity and total alloy content of ferrous metals.

Introduction

THE primary object of most of the determinations of thermal conductivity of metals made in the past has been to correlate thermal and electrical conductivities of the metals. There have been

Publication approved by Director of the Bureau of Standards, United States Department of Commerce.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The authors are respectively assistant metallurgist and metallurgist, U. S. Bureau of Standards, Washington, D. C. Manuscript received July 31, 1933.

comparatively few determinations of the thermal conductivity of irons and steels, the most widely used of all metals. While the thermal conductivity of a structural metal may seldom be the most important factor to be considered in selection or design, the thermal conductivity of structural materials over a range of temperature is of considerable importance in many instances.

This paper describes the apparatus and method used and gives the results obtained in the determinations of the thermal conductivities of a number of metals over a range of temperature between 0 and 600 degrees Cent. (1110 degrees Fahr.).

The materials included several pure metals and a number of ferrous and nonferrous alloys selected as typical examples of commercial materials used for a variety of purposes, and which were known to have considerably different thermal conductivities.

Test Method

The apparatus used was designed by M. S. Van Dusen of the Heat Transfer Section of the Bureau of Standards. It was designed for comparative measurements, thus eliminating calorimetric or power-input determinations which are difficult to perform with uniformly high accuracy over a broad range of temperature. High purity lead was used, either directly or indirectly, as the "standard" with which other metals were compared. The thermal conductivity of lead at ordinary temperatures is believed to be known with as high an accuracy as that of any metal.

The method consists essentially in measuring the axial temperature gradients in two cylindrical bars, soldered together end to end. One end of the system is heated, and the other is cooled. The convex surface of the bars is protected from loss or gain of heat by a shield tube. After a steady state of heat flow is attained, the heat flux is the same in both bars, and the conductivity at any point in either bar is inversely proportional to the temperature gradient at that point. If the absolute value of the conductivity of the metal of one bar is known, at some temperature within the experimental range, the conductivity of the other metal can be calculated at all points where the temperature gradient has been measured.

Fig. 1 is a cross section drawing of the apparatus with test specimens in place. The specimen (A), a round bar 2 centimeters in diameter by 15 centimeters in length, is soldered to the copper

block (C); the "standard" bar (B) also 2 centimeters in diameter but 5 centimeters in length is soldered to the top of the specimen and a brass water chamber (J) is soldered to the top of the standard bar. The shield tube (D) is a chromium-nickel stainless steel

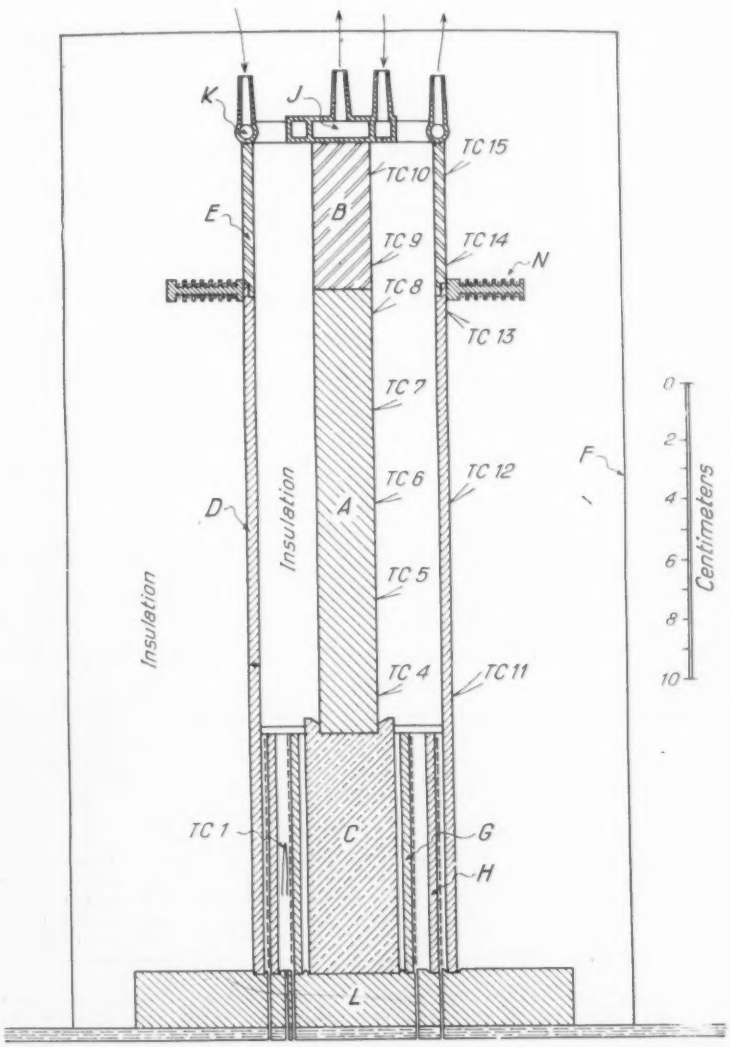


Fig. 1—Cross Section Drawing of Thermal Conductivity Apparatus.

(18-8), the top of which is lap jointed and soldered to the nickel tube (E). A small copper water tube (K) is soldered around the top of the nickel tube. The copper block (C) is heated by resistance ribbon wound around a thin-walled alundum tube (G) and the shield tube (D) is heated at its base, by resistance ribbon wound around the porcelain tube (H). A ring-shaped copper block (N), soldered

to the shield tube at the lap joint between the steel and the nickel, is wound with resistance wire on top and bottom through spiral grooves in the block. Tube (D), coils (G) and (H) and copper block (C) rest on a disk-shaped alundum base (L). The apparatus and base are surrounded by a sheet steel case (F). The space between the bars and shield tube and between the shield tube and case is filled with diatomaceous earth to the top of the case.

Thermocouple 1 was placed between the heating coils (G) and (H) to facilitate adjustment of the supply of heat to the apparatus. Thermocouples 4, 5, 6, 7 and 8 were attached at points about 3 centimeters apart on the specimen (A), by electric welding or by peening. The latter method was found to be more practical on all except the hard or brittle metals. Thermocouples 9 and 10 were attached in the same manner to bar (B). Thermocouples 11, 12, 13, 14 and 15 were attached by peening to the shield tubes directly opposite thermocouples 4, 6, 8, 9 and 10, respectively.

Materials

The nonferrous metals on which determinations were made are described in Table I, and the irons and steels in Table II.

Table I
Chemical Composition and Previous History of Nonferrous Materials

Specimen	Material	Per Cent Ni[1]	Cr	Fe	Co	Cu	Mn	Si	Al	Pb	Zn	S	C	
N_2	Alumel	95	..	.....	.....	.....	2.0	1.0	2.0	....	.....	.....	.....	*
N_3	Chromel P	90	10	.....	.....	.....	....	.....	...	....	.....	.....	.....	
N_4	Chromel A	80	20	.....	.....	.....	....	.....	...	....	.....	.....	.....	
N_5	Chromel C	61	16	23	.....	.....	....	.....	...	....	.....	.....	.....	
N_6	Chromel 502	34	10	56	.....	.....	....	.....	...	....	.....	.....	.....	
N.S.	Nickel	99+	..	0.60	.....	0.14	0.09	.....	...	....	.....	0.014	.....	**
N_1	Nickel	99.94	..	0.03	0.016	0.006	....	0.006	...	....	.....	0.004	0.005	†
Z.S.	Zinc	.....	..	0.02	.....	.....	....	.....	...	0.04	99.9+	.....	.....	‡
L.S.	Lead	.....	..	.....	.....	.....	....	.....	...	....	.....	.....	.....	¶

*Pouring temperature approximately 2800 degrees Fahr. Cast in 5-inch diameter ingots. Ingots heated to 2300 degrees Fahr. and hot-rolled to 1⅝-inch square billets. N_2, N_3 and N_6 billets hot-rolled to ¾-inch diameter round bars. Specimens machined and tested in "as rolled" condition. Chemical compositions "nominal."

**Commercial malleable nickel.

†High purity nickel, melted in Arsem furnace. Furnace cooled.

‡"C.P." Zinc specimen melted and cast in graphite. Cadmium not detected by chemical analysis.

¶Bureau of Standards melting point standard lead. Specimen melted in graphite and cast in bottom feed cast iron mold. Purity indicated by freezing point of 327.4 degrees Cent. Chemical analysis not made.

[1]Nickel plus cobalt.

Results

The results of the thermal conductivity determinations on the materials listed in Tables I and II are shown graphically in Figs. 2 to 9, inclusive. The value for the thermal conductivity of lead at

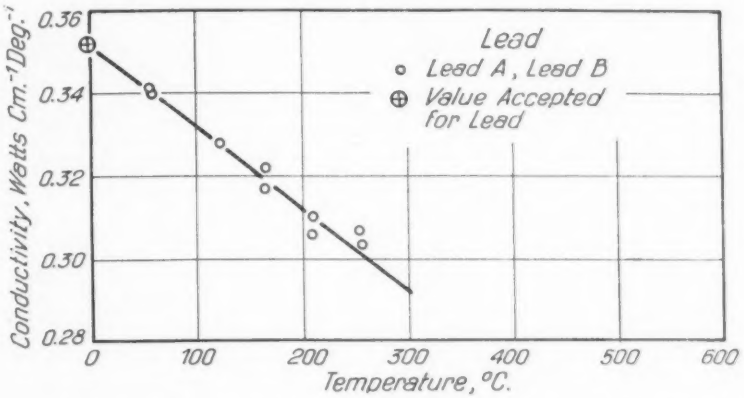


Fig. 2—Thermal Conductivity of Lead from 0 to 300 Degrees Cent. (570 Degrees Fahr.).

0 degree Cent., 0.352 watts cm^{-1} deg^{-1} (International Critical Tables, Volume II, page 218) was used as the basis for all values of conductivity given in absolute units.

The change in conductivity of lead with change in temperature was determined in the range 60 to 250 degrees Cent. (140 to 480

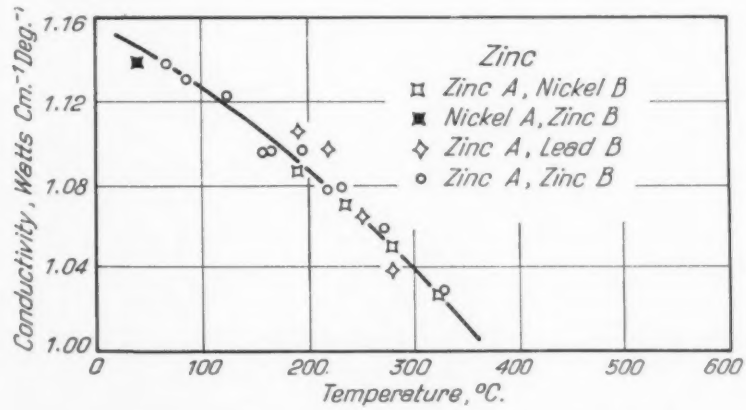


Fig. 3—Thermal Conductivity of Zinc from 25 to 350 Degrees Cent. (660 Degrees Fahr.).

degrees Fahr.). The results are plotted in Fig. 2. Comparisons were also made between lead and zinc, between lead and malleable nickel and between zinc and malleable nickel. These comparisons

Table II
Chemical Composition and Previous History of Materials

No.	Material	Chemical Composition—Per Cent T.C.	G.C.	C.C.	C	Mn	P	S	Si	Ni	Cr	W	Al	Ti	Remarks
C_1	Basic open-hearth iron	.....	.....	.....	0.02	0.03	0.042	0.005	.....	.....	.....	....	....	....	Hot rolled to 1.0-inch bar. Tested "as rolled."
C_2	Wrought iron	... .	.....	.....	0.04	0.046	0.136	0.025	0.265	.....	.....	....	....	....	Hot rolled to 1.0-inch bar. Grade A. A.S.T.M. A 84-21. Tested in the direction of rolling "as rolled."
C_3	Cast iron	3.93	3.34	0.59	.....	0.63	0.134	0.077	1.40	.....	.....	....	....	....	Ingot mold material from cupola. Machined from a sand-cast bar 1.11-inch diameter and tested in the "as cast" condition.
C_4	Cast iron	4.16	3.50	0.66	.....	0.79	0.120	0.040	1.35	.....	.....	....	....	....	Ingot mold material from blast furnace. Machined from a sand-cast bar 1.11-inch diameter and tested in the "as cast" condition.
S_1	High carbon steel	.....	.....	.....	0.83	0.27	0.017	0.015	0.16	.....	.....	....	....	....	Specimen machined from hot-rolled rod 1.0-inch in diameter. Bar was heated to 800 degrees Cent. for 2 hours in an electric furnace and furnace cooled.
S_1Q	Same	.... .	.....	.....	0.83	0.27	0.017	0.015	0.16	.....	.....	....	....	....	After the thermal conductivity determination, specimen S_1 was normalized by heating to 900 degrees Cent. for 10 minutes and air cooled. Reheated to 800 degrees Cent. 10 minutes quenched in water at room temperature. Reheated to 250 degrees Cent. 1 hour, furnace cooled.
S_2	Low nickel steel	.....	.....	.....	0.35	0.56	0.015	0.020	0.02	1.37	0.46	....	....	....	Basic open-hearth steel, poured at 1480 degrees Cent. to an 18x21-inch ingot. Hot rolled to 4x4 inches, then to a rod 1 inch in diameter. Normalized at 900° C.
S_3	Low manganese steel	.....	.....	.....	0.51	1.65	0.016	0.023	0.24	0.10	.....	....	....	....	Basic open-hearth steel, poured at 1480 degrees Cent. to a 22x25-inch ingot. Hot rolled to 4x4 inches, then to a rod, 1 inch in diameter. Normalized at 900° C.
S_4	Tungsten steel	.....	.....	.....	0.35	0.75	0.35	0.028	0.22	0.17	0.61	1.04	....	....	Acid open-hearth steel, poured at 1490 degrees Cent. to an 18x21-inch ingot. Hot rolled to 4x4 inches, then to a rod 1 inch in diameter. Normalized at 900° C.

S_3	Low manganese steel	.....	.....	.....	.....	0.51	1.65	0.016	0.023	0.24	0.10	.....	.....	.....	.....	.....	Basic open-hearth steel, poured at 1480 degrees Cent. to a 22x25-inch ingot. Hot rolled to 4x4 inches, then to a rod, 1 inch in diameter. Normalized at 900° C.
S_4	Tungsten steel	.....	.....	.....	.....	0.35	0.75	0.35	0.028	0.22	0.17	0.61	1.04	.....	.....	.....	Acid open-hearth steel, poured at 1490 degrees Cent. to an 18x21-inch ingot. Hot rolled to 4x4 inches, then to a rod 1 inch in diameter. Normalized at 900° C.
S_5	Low chromium steel	.....	.....	.....	.....	0.10	0.45	0.013	0.017	0.18	....	5.15	.....	.....	.....	.....	Hot rolled to 1½-inch round bar. Annealed.
		.....	.....	.....	.....	0.08	0.35	0.020	0.017	0.20	0.05	15.19	.....	.....	.....	.....	Basic electric furnace steel poured at 1490 degrees Cent. to a 12x12-inch ingot. Cogged to 4x4 inches, then rolled to a 1-inch round bar. Annealed at 845 degrees Cent.
A_1	Chromium steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.07	0.09	0.015	0.010	0.09	0.23	12.00	.....	.....	.....	.....	Basic electric furnace steel poured at 1500 degrees Cent. to an 8x8-inch ingot. Cogged to 4x4 inches, then rolled to a 1-inch round bar. Annealed at 845 degrees Cent.
A_2	Chromium steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.14	0.19	0.020	0.015	0.12	0.70	14.60	.....	.....	.....	.....	Basic electric furnace steel poured at 1500 degrees Cent. to an 8x8-inch ingot. Cogged to 4x4 inches, then rolled to a 1-inch round bar. Annealed at 845 degrees Cent.
A_3	Chromium steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.10	0.40	0.013	0.008	0.45	0.18	26.00	.....	.....	.....	.....	Hot rolled to 1½-inch round bar. Annealed.
A_4	High chromium steel	.....	.....	.....	.....												
		.....	.....	.....	.....	1.10	0.30	.....	.....	0.47	0.35	17.12	.....	1.55	.....	.....	500-lb. induction furnace. Poured at 1490 degrees Cent. to 8x8-inch ingot. Rolled to 4x4 inches, then to a 1-inch round bar. Normalized at 900 degrees Cent.
A_5	Chromium-aluminum steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.70–0.80	12.–13.	.....	.....	.....	3.00	.....	.....	.....	.....	.....	Machined specimen received. Previous history unknown. (Chemical composition nominal.)
A_6	Manganese-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.07	0.27	.....	.....	.....	9.10	18.6	.....	.....	.....	.....	1-inch round bar. Heated to 735 degrees Cent., held for 8 hours and cooled in diatomaceous earth.
A_7	Chromium-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.11	0.19	.....	.....	.....	9.21	18.5	.....	.....	.....	.....	1-inch round bar. Heated to 1120 degrees Cent. and quenched in cold water.
A_8	Chromium-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.24	0.37	.....	.....	.....	8.96	19.6	.....	.....	.....	.....	1-inch round bar. Heated to 735 degrees Cent., held for 8 hours and cooled in diatomaceous earth.
A_9	Chromium-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.24	0.28	.....	.....	.....	7.99	19.6	.....	.....	.....	.....	1-inch round bar. Heated to 1120 degrees Cent., water quenched.
A_{10}	Chromium-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.24	0.28	.....	.....	.....	7.99	19.6	.....	.....	.....	.....	After the thermal conductivity determination, specimen A_{10} was heated for 8 hours at 735 degrees Cent. and furnace cooled.
$A_{10}A$	Chromium-nickel steel	.....	.....	.....	.....												
		.....	.....	.....	.....	0.07	0.59	0.013	0.003	0.47	9.12	18.08	.....	.....	.....	0.34	Hot rolled 1½-inch round bar. Annealed.
A_{11}	Chromium-nickel-titanium steel	.....	.....	.....	.....												

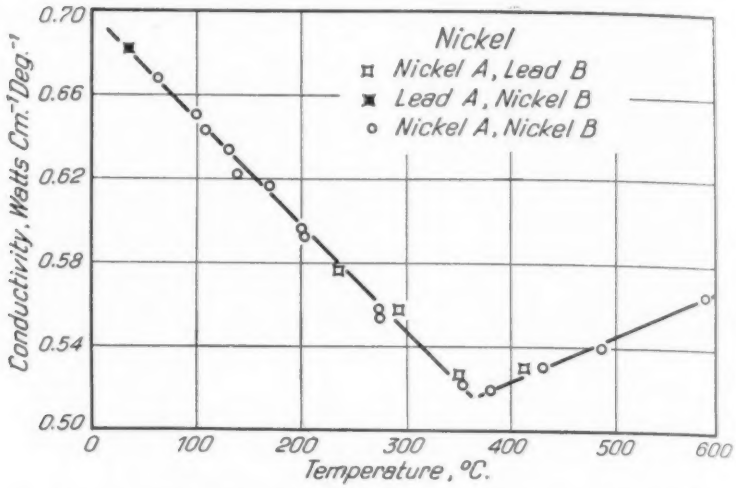


Fig. 4—Thermal Conductivity of Commercially Pure Nickel from 25 to 600 Degrees Cent. (1110 Degrees Fahr.).

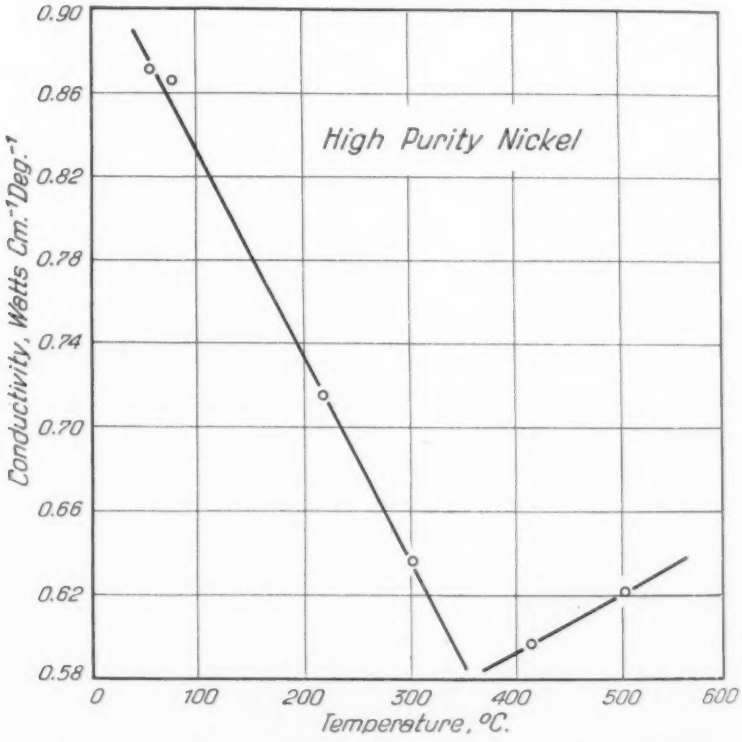


Fig. 5—Thermal Conductivity of High Purity Nickel from 25 to 550 Degrees Cent. (1020 Degrees Fahr.).

permitted an estimation of the experimental error. The values for the thermal conductivity of zinc at various temperatures from 40 to 330 degrees Cent. (105 to 625 degrees Fahr.) obtained from these

comparisons are plotted in Fig. 3. The values obtained in a like manner for the thermal conductivity of malleable nickel from 40 to 600 degrees Cent. (105 to 1110 degrees Fahr.) are plotted in Fig. 4. The results on the specimen of high purity nickel are shown in Fig. 5. The results with the nickel alloys are grouped in Fig. 6; those on the irons and low alloy steels, in Fig. 7; those on the high

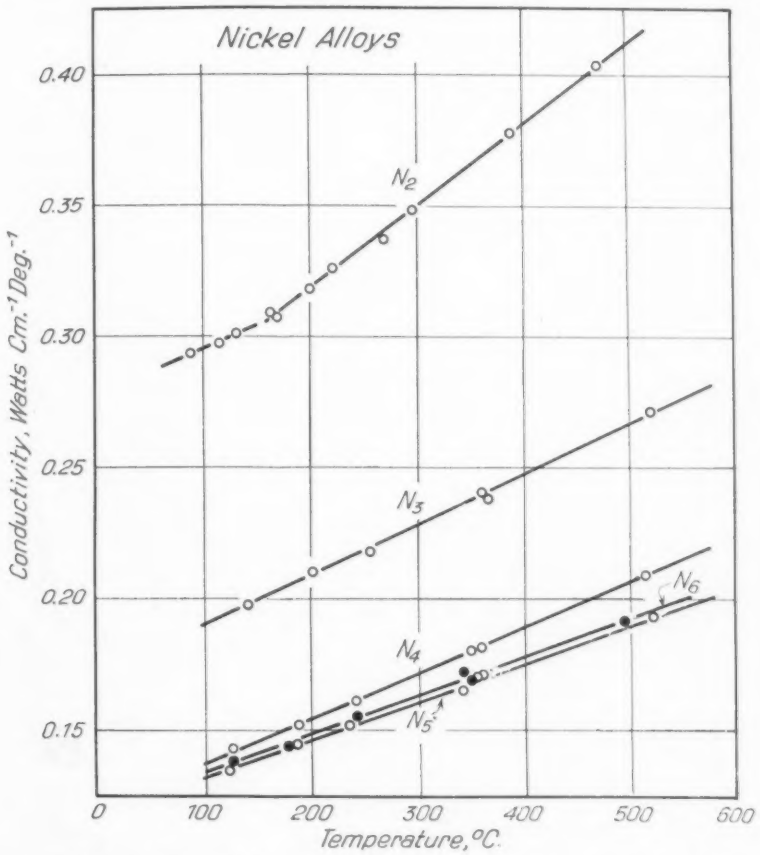


Fig. 6—Thermal Conductivity of Nickel Alloys from 100 to 550 Degrees Cent. (1020 Degrees Fahr.).
N_2—95 per cent Nickel; 2 per cent Aluminum; 2 per cent Manganese; 1 per cent Silicon.
N_3—90 per cent Nickel; 10 per cent Chromium.
N_4—80 per cent Nickel; 20 per cent Chromium.
N_5—61 per cent Nickel; 16 per cent Chromium; 23 per cent Iron.
N_6—34 per cent Nickel; 10 per cent Chromium; 56 per cent Iron.

alloy steels in Fig. 8 and on the "18-8" stainless steels in Fig. 9 with the exception that the curve for a titanium bearing "18-8" stainless steel (specimen A_{11}) is given in Fig. 8.

The values represented by the curves in Figs. 2 to 9 are believed to be accurate relative to lead to within 2 per cent. The values for lead are probably correct to within 3 per cent.

Thermal conductivities in watts cm^{-1} deg^{-1} interpolated for even hundreds of degrees from the experimental results for all of the materials tested are listed in Table III.

Table III

Thermal Conductivity in Watts cm^{-1} deg^{-1}, Interpolated from Experimental Results[1]

Material		Degrees Centigrade 100	200	300	400	500
(L.S.)	Lead	0.332	0.312	.....	.....	.....
(Z.S.)	Zinc	1.127	1.088	1.036	.....	.....
(N.S.)	Nickel	0.649	0.599	0.549	0.524	0.546
(N_1)	Nickel	0.828	0.732	0.638	0.593	0.621
(N_2)	Alumel	0.296	0.318	0.350	0.381	0.412
(N_3)	Chromel P	0.190	0.209	0.228	0.247	0.266
(N_4)	Chromel A	0.136	0.154	0.172	0.189	0.206
(N_5)	Chromel C	0.132	0.147	0.161	0.175	0.190
(N_6)	Chromel 502	0.134	0.149	0.163	0.177	0.192
C_1	Basic open-hearth iron	0.665	0.607	0.549	0.491	0.435
C_2	Wrought iron	0.589	0.543	0.497	0.451	0.405
C_3	Cast iron	0.550	0.519	0.488	0.458	0.426
C_4	Cast iron	0.528	0.502	0.476	0.449	0.422
S_1	Plain carbon steel	0.458	0.435	0.413	0.390	0.367
S_1Q	Same, quenched	0.412	0.408	0.396	0.381	0.364
S_2	Low nickel steel	0.445	0.427	0.409	0.391	0.372
S_3	Low manganese steel	0.403	0.389	0.376	0.363	0.349
S_4	Tungsten steel	0.385	0.371	0.363	0.352	0.341
S_5	Low chromium steel	0.366	0.358	0.351	0.343	0.336
A_1	Chromium steel	0.261	0.262	0.262	0.262	0.263
A_2	Chromium steel	0.249	0.259	0.268	0.277	.....
A_3	Chromium steel	0.243	0.247	0.252	0.256	0.261
A_4	High chromium steel	0.209	0.219	0.229	0.238	0.243
A_5	Chromium-aluminum steel	0.177	0.188	0.199	0.210	0.221
A_6	Manganese-nickel steel	0.148	0.160	0.171	0.183	0.195
A_7	Chromium-nickel steel	0.164	0.177	0.190	0.203	0.216
A_8	Chromium-nickel steel	0.163	0.176	0.189	0.201	0.214
A_9	Chromium-nickel steel	0.156	0.172	0.187	0.202	0.217
A_{10}	Chromium-nickel steel	0.149	0.164	0.178	0.193	0.207
$A_{10}A$	Same—annealed	0.150	0.166	0.181	0.196	0.212
A_{11}	Chromium-nickel-titanium steel	0.161	0.176	0.191	0.206	0.221

[1] 1 watt cm^{-1} deg^{-1} = 1 watt/(sq.cm.) (deg. C/cm) = 0.239 Cal/(sec) (sq.cm.) (deg. C/cm.).

1 watt cm^{-1} deg^{-1} = 57.9 Btu/(hr) (sq.ft.) (deg. F/ft.).

Discussion

For the pure metals, the irons and low alloy steels, the thermal conductivities decreased with increase in temperature. The conductivities of the high alloy steels and of the nickel alloys increased with increase in temperature. In general, the thermal conductivities of all the materials tested were linear functions of the temperature within the range of temperature in which measurements were made. A notable exception is nickel: the change from a negative to a positive temperature coefficient of thermal conductivity undoubtedly coincided with the magnetic transformation of the nickel which has been reported by various authors to occur at temperatures ranging from 340 to 350 degrees Cent. (645 to 660 degrees Fahr.). A

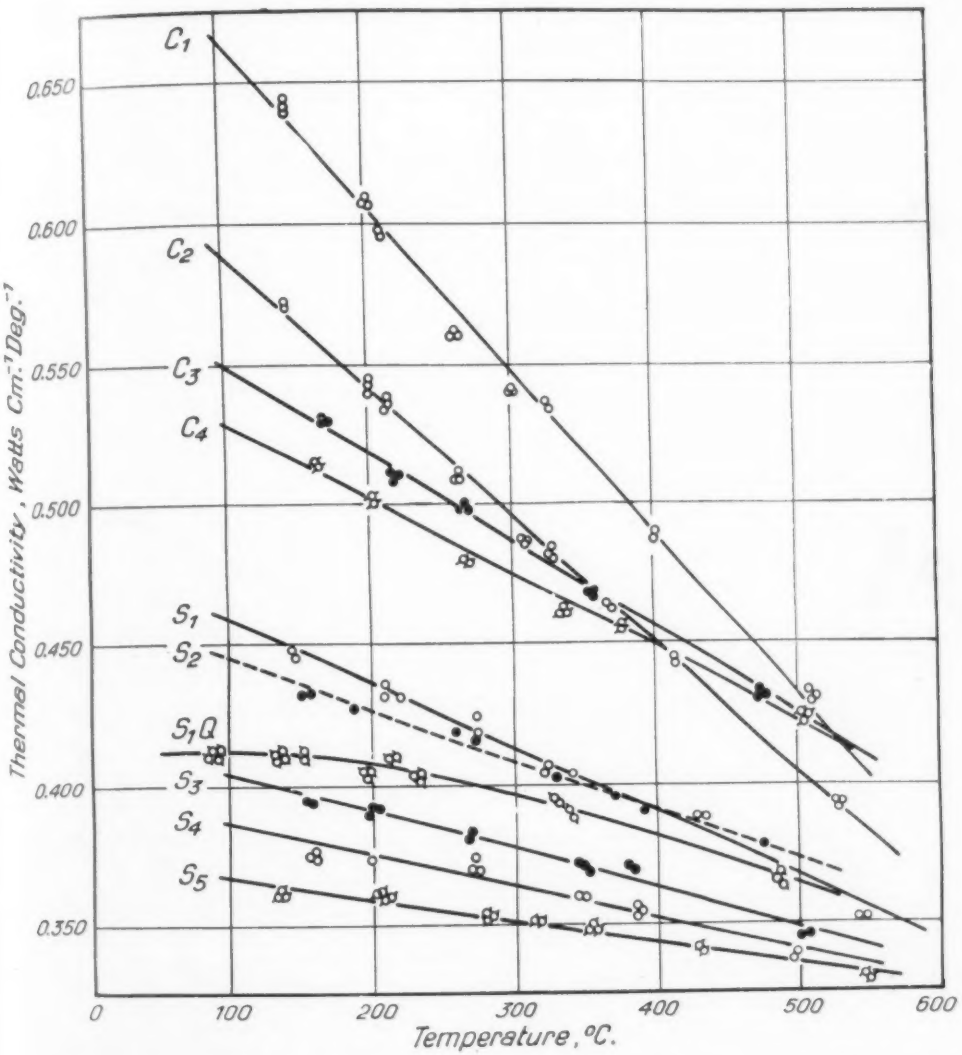


Fig. 7—Thermal Conductivity of Irons and Low Alloy Steels from 100 to 550 degrees Cent. (1020 Degrees Fahr.).
C_1—open hearth iron; approximately 99.9 per cent Iron.
C_2—wrought iron; approximately 99.5 per cent Iron.
C_3 and C_4—Cast irons; approximately 4.0 per cent Carbon and 1.5 per cent Silicon.
S_1 and S_1Q—carbon steel; 0.83 per cent Carbon.
S_2—nickel steel; 0.35 per cent Carbon; 1.37 per cent Nickel; 0.46 per cent Chromium.
S_3—managanese steel; 0.51 per cent Carbon; 1.65 per cent Manganese.
S_4—tungsten steel; 0.35 per cent Carbon; 1.04 per cent Tungsten.
S_5—chromium steel; 0.10 per cent Carbon; 5.15 per cent Chromium.

number of measurements were made on the commercially pure nickel specimen N.S. in an attempt to narrow the range at which the change in conductivity took place. As shown in Figs. 4 and 5 the change in both the commercial nickel and the high purity nickel occurred between 350 and 365 degrees Cent. (660 and 690 degrees Fahr.).

A small and somewhat indefinite change in the temperature

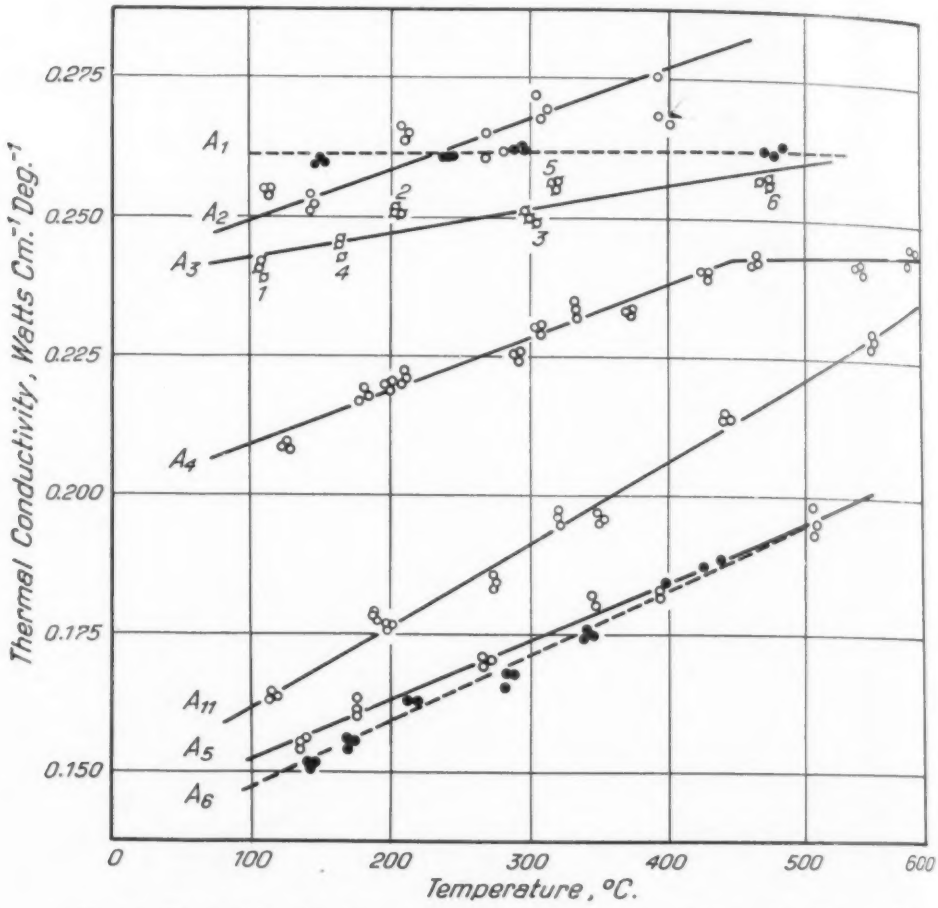


Fig. 8—Thermal Conductivity of High Alloy Steels from 100 to 600 Degrees Cent. (1110 Degrees Fahr.).

A_1—Chromium steel; 0.08 per cent Carbon; 15.19 per cent Chromium.
A_2—Chromium steel; 0.07 per cent Carbon; 12.0 per cent Chromium.
A_3—Chromium steel; 0.14 per cent Carbon; 14.60 per cent Chromium.
A_4—Chromium steel; 0.10 per cent Carbon; 26.00 per cent Chromium.
A_5—Chromium-aluminum steel, 1.10 per cent Carbon; 1.55 per cent Aluminum; 17.12 per cent Chromium.
A_6—Manganese-nickel steel; 0.7 to 0.8 per cent Carbon; 12 to 13 per cent Manganese; 3.0 per cent Nickel.
A_{11}—Titanium bearing "18-8" Stainless; 0.07 per cent Carbon; 0.34 per cent Titanium.

coefficient of thermal conductivity was also found in the nickel alloy "Alumel" containing 95 per cent nickel (Specimen N_2, Fig. 6). This change also probably was coincident with the magnetic transformation of the alloy, although it occurred at a lower temperature than for pure nickel.

The experimental results for zinc as shown in Fig. 3 indicated that the conductivity-temperature relation was not represented by a straight line. The only other exception to the straight line relation between conductivity and temperature was the plain carbon

steel in the quenched condition, Specimen S_{1Q}. The change in temperature coefficient of thermal conductivity as shown by the curved line in Fig. 7 was undoubtedly caused by the tempering of the specimen while the tests were in progress.

For the iron alloys, the effect of small differences in composition on the thermal conductivity is more marked in the alloys containing a small amount of alloying constituents than in the alloys with higher alloy concentrations.

An additional and somewhat complicating factor is the nature of the alloy. For example, the total alloy content of cast iron (C_3) is greater than the alloy content of the plain carbon steel (S_1), but the thermal conductivity at 100 degrees Cent. of the cast iron was found to be approximately 20 per cent higher than the conductivity of the plain carbon steel at the same temperature. The results on the plain carbon steel (S_1 and S_{1Q}) show that a heat treatment which resulted in a change in structural constitution produced an appreciable change in conductivity at lower temperatures.

An unusual "scatter" is noticeable in the plotted points representing the determinations on the chromium steel (A_2, Fig. 8). The differences are irregular in character and the most probable explanation is that a structural change in the specimen took place with

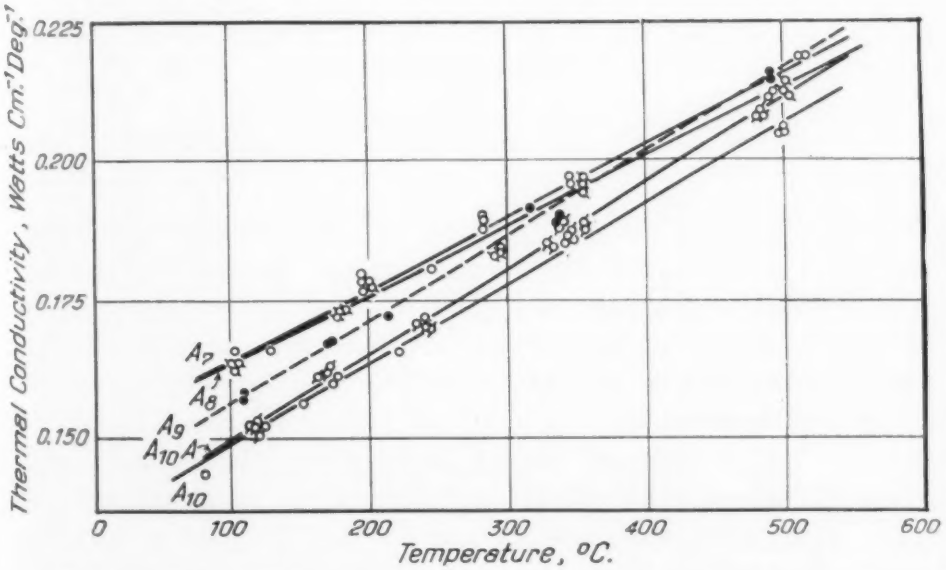


Fig. 9—Thermal Conductivity of "18-8" Stainless Steels from 100 to 550 Degrees Cent. (1020 Degrees Fahr.).
A_7—0.07 per cent Carbon; 9.10 per cent Nickel; 18.6 per cent Chromium.
A_8—0.11 per cent Carbon; 9.21 per cent Nickel; 18.5 per cent Chromium.
A_9—0.24 per cent Carbon; 8.96 per cent Nickel; 19.6 per cent Chromium.
A_{10} and A_{10A}—0.24 per cent Carbon; 7.99 per cent Nickel; 19.6 per cent Chromium.

repeated heating in the apparatus. The irregular character of the "scatter" supports the belief that it cannot be attributed to experimental error. A typical example of "scatter" evidently due to experimental error or to a lack of homogeneity of the specimen is shown by the points representing the determinations on steel A_2. The results of the first series of determinations at relatively low temperatures are represented by the groups of points numbered 1,

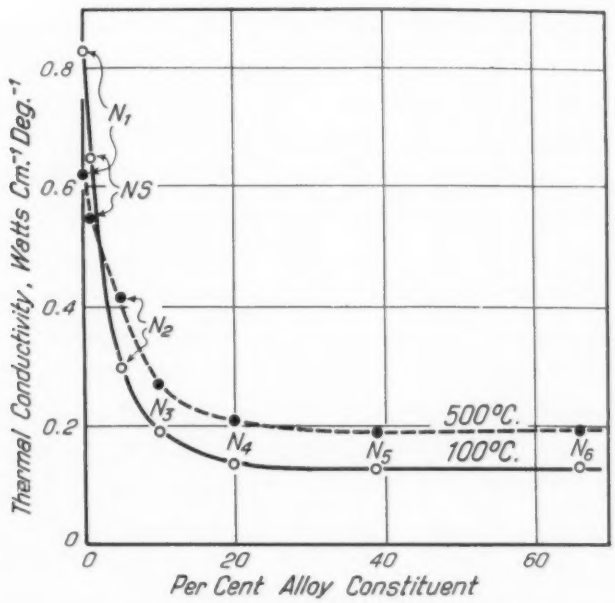


Fig. 10—Decrease in Thermal Conductivity of Nickel at 100 and 500 Degrees Cent. (930 Degrees Fahr.), with Increase in Amount of Alloying Elements Aluminum, Chromium and Iron.

2 and 3 (Fig. 8). The results of the second series at relatively high temperatures are represented by the groups, 4, 5 and 6. The character of the "scatter" is the same for both series, although the temperatures were quite different. A more complete investigation over a wider range of temperature is desirable but was not possible in the present apparatus.

The results obtained on the nickel base alloys, "alumel and chromel," indicated that the thermal conductivity of nickel decreased fairly regularly as the total amount of alloying elements added to nickel was increased, as shown in Fig. 10, in which conductivities at both 100 and 500 degrees Cent. (210 and 930 degrees Fahr.) are plotted. Likewise, Fig. 11 shows that there was some regularity to the decrease in the conductivity of iron, at both 100 and 500 degrees Cent.

(210 and 930 degrees Fahr.), as the amount of chromium alloyed with the iron was increased.

Nevertheless, the many, and sometimes conflicting, factors make it practically impossible to generalize concerning the quantitative relationship of thermal conductivity and total alloy content of ferrous metals from tests made on a miscellaneous collection of alloys.

The "18-8" chromium-nickel steels studied represent low carbon steels (0.07 to 0.11 per cent carbon) in the annealed condition (A_7) and in the quenched condition (A_8) and high carbon steel (0.24 per cent) in the corresponding conditions, annealed (A_9) and

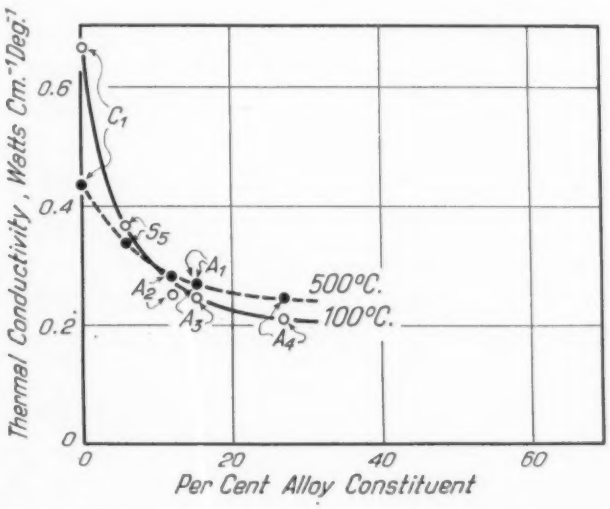


Fig. 11—Decrease in Thermal Conductivity of Iron at 100 and 500 Degrees Cent. (930 Degrees Fahr.) with Increase in Amount of Chromium.

quenched (A_{10}). As shown by the curves in Fig. 9, the results on the two low carbon steels coincided within the experimental error at low temperatures, and very nearly so at higher temperatures. The higher carbon specimens showed differences in both thermal conductivity and temperature coefficient over the whole temperature range. A greater difference in composition existed between the two high carbon steels than between the two low carbon steels. In order to determine whether the differences in thermal conductivity of the high carbon steels could be attributed to composition or to previous heat treatment, the quenched specimen was annealed and the thermal conductivity redetermined. According to the results, the thermal conductivity of the re-annealed steel ($A_{10}A$) was unchanged at low temperature, but at higher temperatures the annealed material had a

higher conductivity than the quenched material. It is noteworthy, and possibly of some significance, that the thermal conductivity of the annealed steel was practically the same as that in the quenched state, but the temperature coefficient of the re-annealed specimen ($A_{10}A$) was of the same order of magnitude as that of the annealed specimen (A_9) of a different composition.

Summary

1. An apparatus and method for the determination of the thermal conductivity of metals is described. Results are given for the determinations of thermal conductivities of a number of metals over a temperature range between 0 and 600 degrees Cent. (1110 degrees Fahr.). The materials included the pure metals, lead, zinc and nickel; a number of commercial nickel-base alloys and twenty irons and steels selected as typical examples of commercial materials used for a variety of purposes and which were known to have considerably different thermal conductivities. The data on the chromium-iron and chromium-nickel-iron alloys are of particular interest because of the lack of previous data on the thermal conductivity of "stainless" steels.

2. The apparatus was designed for comparative measurements and thus eliminated calorimetric or power-input determinations which are difficult to perform with uniformly high accuracy over a broad range of temperature. High purity lead was used, either directly or indirectly, as the standard with which other metals were compared.

3. The results obtained on the various materials are plotted on curves. Thermal conductivities in watts cm^{-1} deg^{-1} interpolated in increments of temperature of 100 degrees from 100 to 600 degrees Cent. (210 to 1110 degrees Fahr.) are tabulated.

4. For the pure metals, the irons and low alloy steels, the thermal conductivities decrease with increase in temperature. The conductivities of the high alloy steels and of the nickel alloys increase with increase in temperature. In general, the thermal conductivities of all the materials tested are linear functions of the temperature within the range within which measurements were made. A noteworthy exception is nickel: a sharp change from a negative to a positive temperature coefficient of thermal conductivity occurs at the temperature of the magnetic transformation.

5. For the ferrous alloys, an increase in the amount of alloying

constituents in iron caused, in general, an increase in the temperature coefficient of thermal conductivity. However, the many, and sometimes conflicting, factors concerned make it practically impossible to generalize concerning the quantitative relationship of thermal conductivity and total alloy content of ferrous metals.

Acknowledgment

Grateful acknowledgment is made to M. S. Van Dusen, of the Heat Transfer Section of the Bureau of Standards, under whose supervision the experimental work was done, and to the following organizations for supplying many of the materials. The nickel alloys were furnished by the Hoskins Manufacturing Co.; the 5 per cent chromium and the titanium bearing "18-8" stainless steels were furnished by the Research Laboratory of the United States Steel Corporation; the manganese-nickel steel was furnished by the Taylor Wharton Iron and Steel Company; the cast irons, the low alloy steels, the chromium and the "18-8" stainless steels were furnished by the Bethlehem Steel Corporation.

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ON GRAIN SIZE AND GRAIN GROWTH

By M. A. Grossmann

Abstract

The paper records observations of the manner in which grain size develops in a carburizing test, and, in particular, the relationship of the McQuaid-Ehn carburizing test (usually carried out at 1700 degrees Fahr. for 8 hours) to the austenite grain sizes which may develop at other temperatures or in other lengths of time.

It was found that when steel is heated to the temperature at which it transforms to austenite, the resulting initial austenite grain size (whatever it may be) remains at first unchanged when the heating is continued, even for considerable periods of time. At some higher temperature, grain coarsening sets in, and it was found that each different lot of steel has its characteristic coarsening temperature.

Low carbon steels usually coarsen by the process of "exaggerated grain growth," wherein certain grains grow to large size, while the balance remain unchanged until they too are absorbed.

In carburizing, the (austenite) grains of the case may be larger or smaller than the austenite grains of the core.

The initial austenite grain size may be influenced by heat treatment, and so may affect the results of a McQuaid-Ehn test.

AMONG the kinds of grain size studied in steels, an important one is the austenite grain size of a piece of steel about to be quenched (hardened). This relationship between grain size and hardening was pointed out by McQuaid and Ehn[1] and has been elucidated thoroughly by Bain.[2] A question of interest now is the manner in which different grain sizes arise, and, in particular, the influences which cause them to vary.

[1]McQuaid, H. W., and Ehn, E. W., *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 67, 1922.

[2]Bain, E. C., Transactions, American Society for Steel Treating, Vol. 20, November, 1932, p. 385-428.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The author, M. A. Grossmann, is research engineer, Illinois Steel Co., South Chicago, Illinois. Manuscript received June 29, 1933.

In seeking to determine austenite grain size, the method commonly employed is the McQuaid-Ehn test. In this test, as is well known, the steel is carburized at about 1700 degrees Fahr. and then cooled slowly, with the result that the excess carbide (beyond the eutectoid) outlines what were the austenite grains in the carburized region, and so indicates their size. The McQuaid-Ehn grain size is usually the same throughout one heat (melt) of steel.

The McQuaid-Ehn test on any particular lot of steel often gives about the same result, irrespective of any cold work, hot work or heat treatment that may have preceded this test. Indeed, the frequency with which one finds this regularity makes the irregularities the more striking, and seems to warrant an inquiry into the manner in which the austenite grains form and grow.

Formation of Austenite in the Absence of Carburizing

It is useful to examine first a plain carbon steel of the low carbon, "carburizing" grade, partly because the influence of other alloys is absent, and partly because (as it happens) the steel examined here exhibits many of the idiosyncrasies which combine to produce "McQuaid-Ehn grain size." The steel was taken from a heat having the following composition:—

	Carbon	Manganese	Phosphorus	Sulphur	Silicon
Steel No. 1	0.15	0.44	0.015	0.019	0.22

Specimens were cut from 5 by 5 inch billets which had been rolled from 21-inch diameter ingots. The steel before treatment had the customary grains of ferrite and islands of pearlite as shown in Fig. 1. Given a McQuaid-Ehn test, the steel showed the grain size illustrated in Fig. 2.[3] Our present question is, then, by what process did the low carbon structure of Fig. 1 develop into the high carbon structure shown in Fig. 2.

Consider first the transformation only, that is, the change of the structure of Fig. 1 to grains of austenite, prior to the increase in carbon due to carburizing. A study of this change is found to shed considerable light on the manner in which McQuaid-Ehn grain size develops. This transformation of the pearlite-ferrite structure into

[3]When the thickness of the carburized case is not very great or when the grain size of the case is large, it may be useful to grind the surface for micro-examination at an angle of 15 to 30 degrees to the carburized surface instead of the customary cross section at 90 degrees. This obviously affords a larger area of case for examination, as was done in this instance.

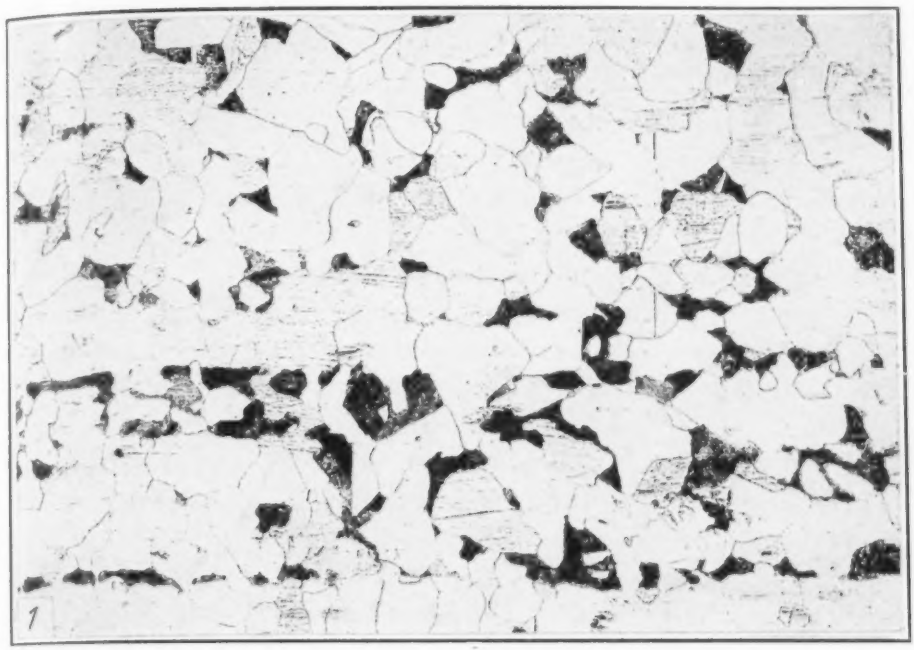


Fig. 1—Steel No. 1. As-received. × 100.

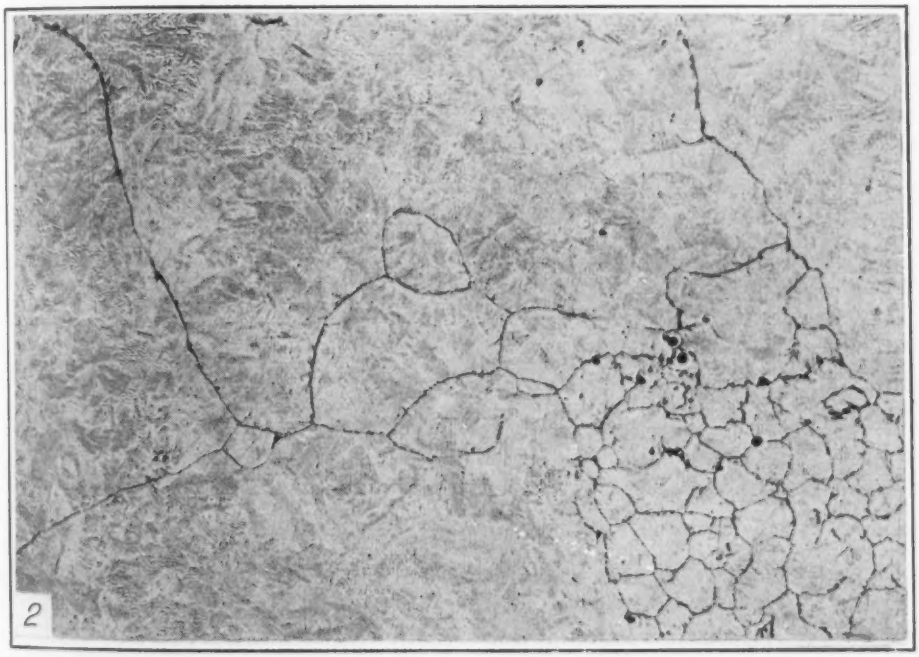


Fig. 2—Steel No. 1. Carburized 8 Hours at 1700 Degrees Fahr. (Sodium Picrate Etch). × 100.

austenite may be traced by means of a gradient heating, followed by quenching. In the present instance, one 6-inch length of the steel was placed in a cold furnace, and the furnace heated (over a period of 1½ hours) in such a way that one end of the piece reached 1315 degrees Fahr., with progressively higher temperatures along the piece, reaching finally a temperature of 1580 degrees Fahr. at the other end of the 6-inch length. A second 6-inch length covered higher temperatures up to 1700 degrees Fahr. The pieces were 6 by 1 by ¼ inch, and when they reached the temperature ranges noted they were quenched in oil. It was thus possible to observe the structures from below the critical range, through this range and up to the 1700 degrees Fahr. carburizing temperature.

Up to the lower critical temperature, the structure remained unaltered, as in Fig. 1, shown at higher magnification in Fig. 3. At a slightly higher temperature, the first change observed was the formation of a small grain of austenite here and there within a pearlite island, as in Fig. 4. We venture to call it a grain of austenite, instead of merely a region of austenite, because there is evidence that each such area is a single grain. This appears when the grain has grown a little further, as in Fig. 5. Here we see a martensitic pattern which extends across the whole of the transformed area, indicating that prior to quenching it had been one single grain of austenite. Fig. 6 shows a structure found quite commonly at this point, including a few of the new austenite grains, some pearlite just in the process of transforming (dark), some untransformed pearlite (lighter) and the original ferrite grains as yet unaffected.

Up to this point the transformation has taken place principally in the pearlite regions. At slightly higher temperatures, austenite begins to encroach into the ferrite grains, as shown in Fig. 7, and proceeds as in Fig. 8, the typical manner of encroachment being indicated by arrows in both figures. Fig. 9 shows some of the newly formed austenite grains, as well as some of the original ferrite grains, as yet untransformed. Figs. 10 and 11 show how the transformation proceeds, until the piece is completely transformed to austenite.

The size of what were the austenite grains is indicated by their borders, and by the extent of the Widmanstatten patterns. It is important to note for subsequent consideration that the size of these austenite grains (Fig. 11) is not unlike that of the original ferrite grains (Fig. 3).

Having thus traced the manner in which the ferrite-pearlite

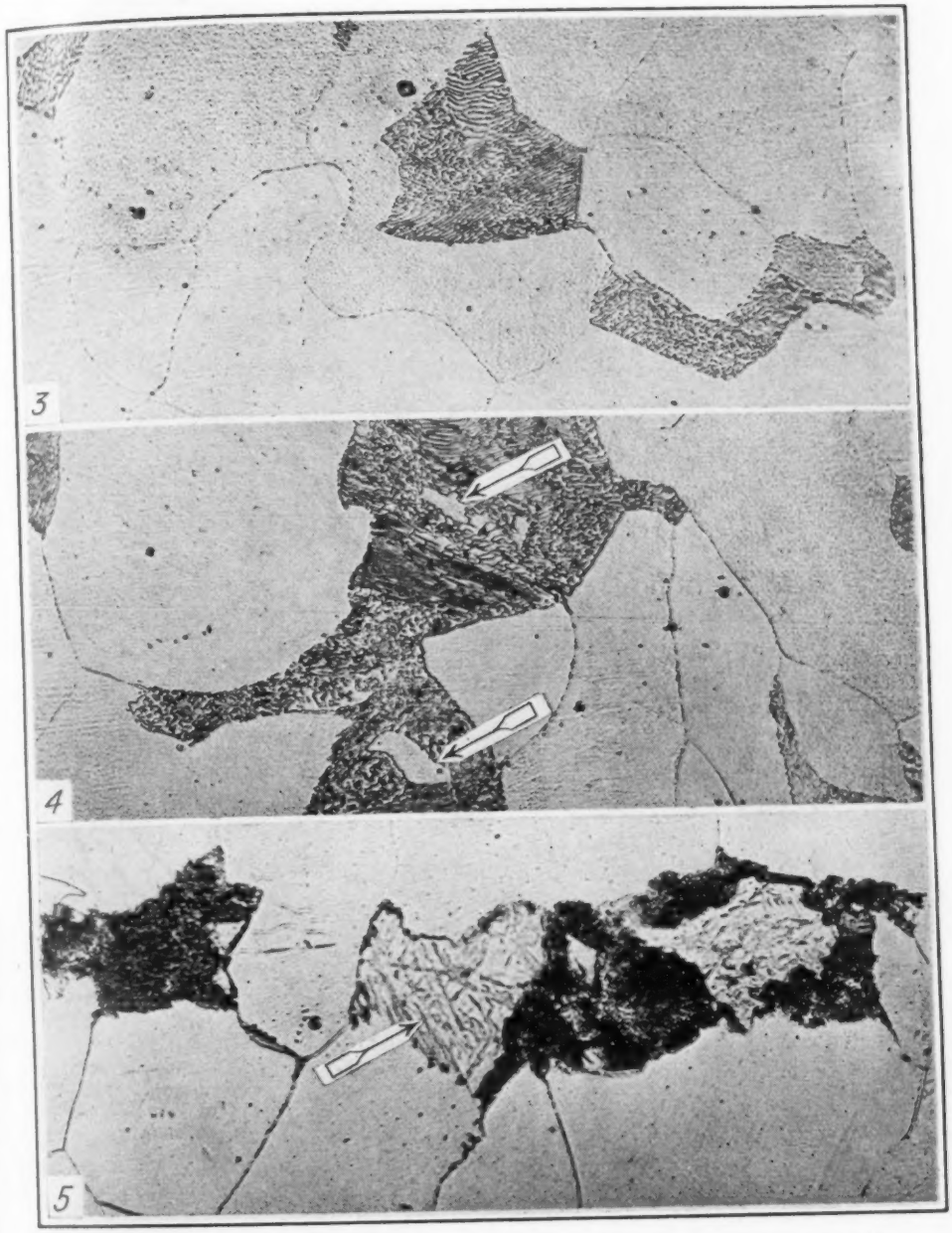


Fig. 3—Steel No. 1. Heated Near the Lower Critical Temperature. × 500.
Fig. 4—Steel No. 1. Heated Near the Lower Critical Temperature. × 500.
Fig. 5—Steel No. 1. Heated Near the Lower Critical Temperature. × 500.

structure of Fig. 1 transforms to austenite, we may turn to our chief interest—the size of these grains. Fig. 12 is the structure already shown at higher magnification in Fig. 11, the sample having been given a mild (oil) quench from 1580 degrees Fahr. Fur-

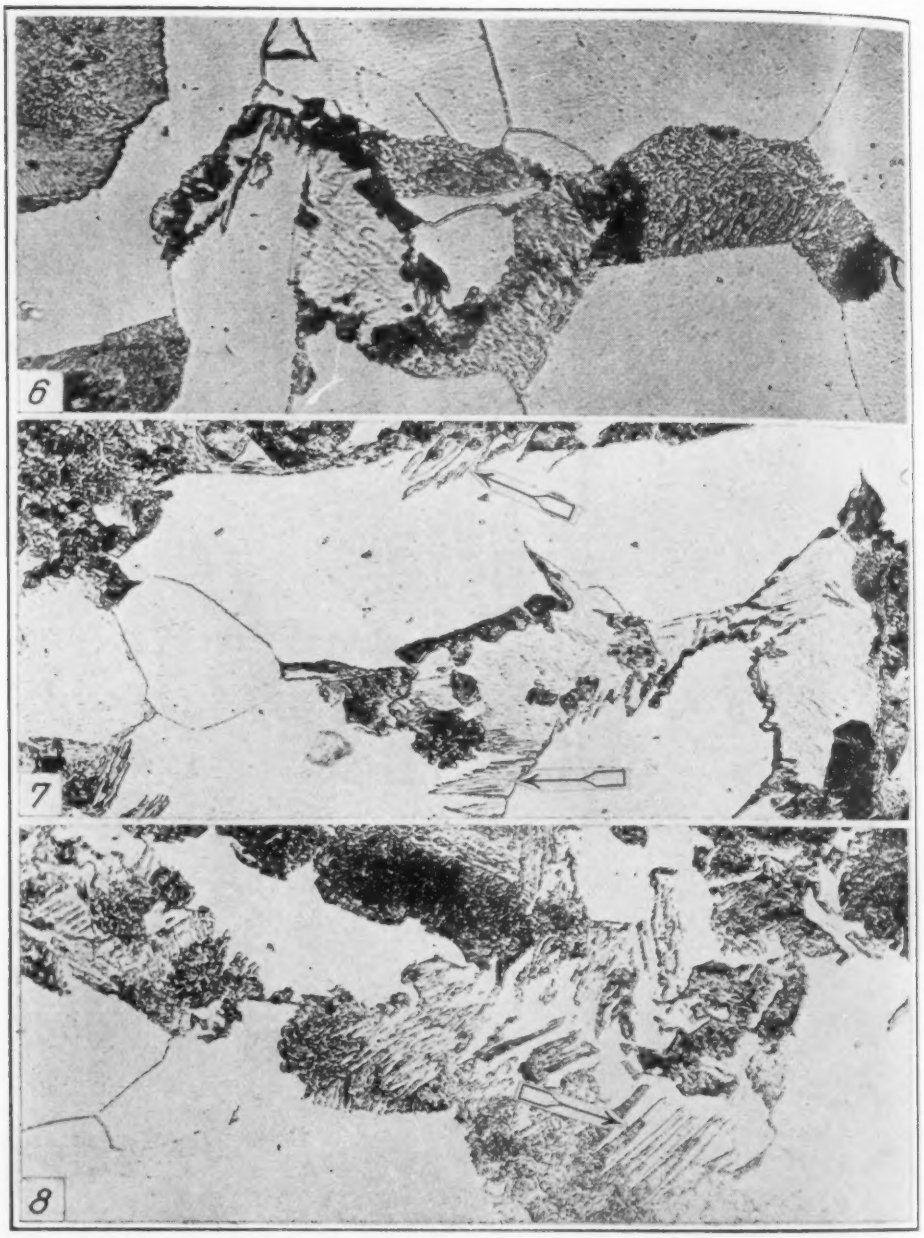


Fig. 6—Steel No. 1. Heated Above the Lower Critical Temperature. × 500.
Fig. 7—Steel No. 1. Heated Above the Lower Critical Temperature. × 500.
Fig. 8—Steel No. 1. Heated Above the Lower Critical Temperature. × 500.

ther, this grain size remained unchanged up to nearly 1700 degrees Fahr. The structure indicates a grain size of about No. 6 on the A. S. T. M. chart. That this was the grain size of the austenite is indicated by the Widmanstatten type of pattern which extends all

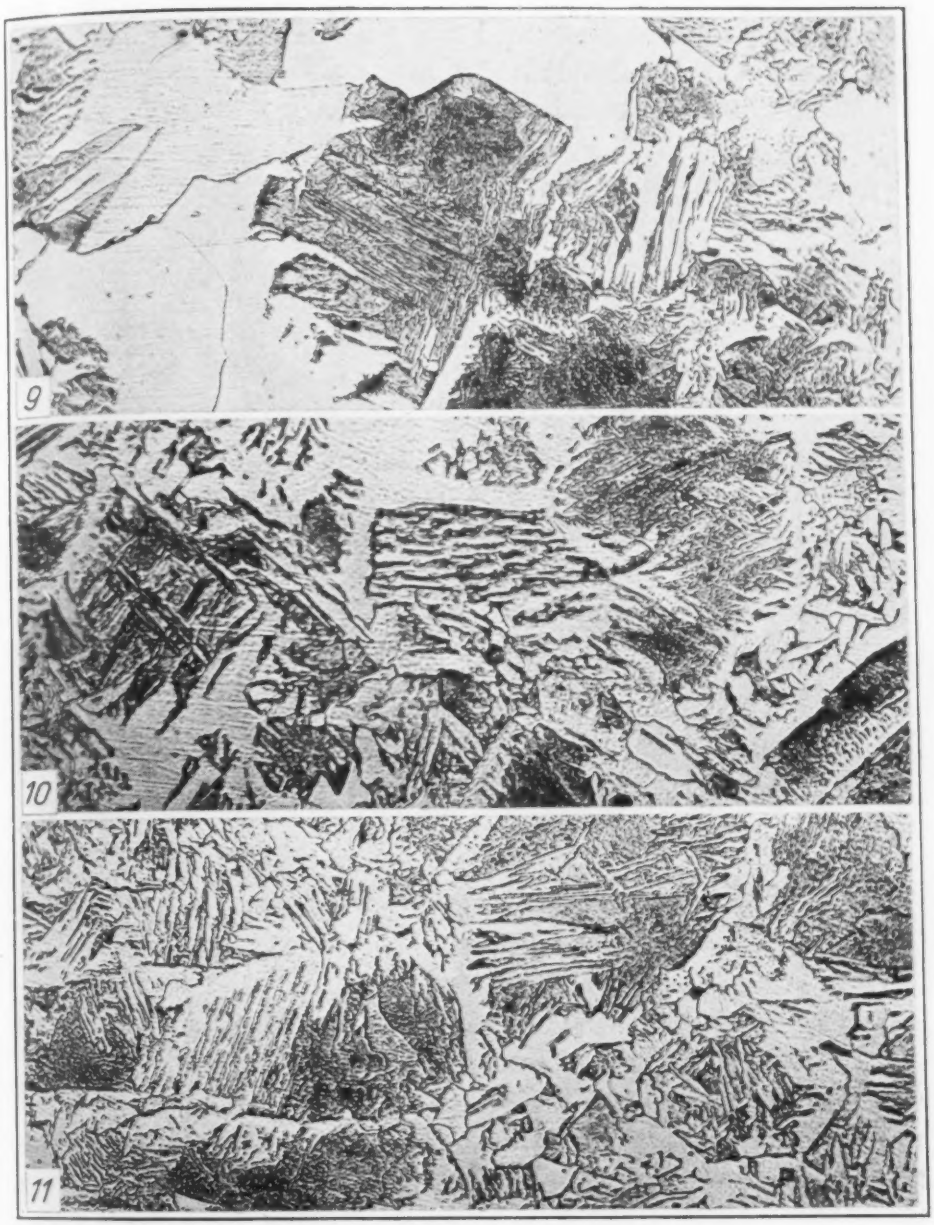


Fig. 9—Steel No. 1. Heated to the Upper Part of the Critical Range. × 500.
Fig. 10—Steel No. 1. Heated to the Upper Part of the Critical Range. × 500.
Fig. 11—Steel No. 1. Heated to the Upper Part of the Critical Range. × 500.

the way across each of the individual grains. Since there might be some question whether this really indicates the size of the austenite grains from which this structure was formed, and since many of the conclusions drawn here hinge on whether the austenite grain size

is actually as indicated, two additional devices were employed in seeking to learn the austenite grain size. Examination of photographs shown by Bain[2] indicated that where ferrite precipitated from austenite in an interrupted quench, it precipitated first at the grain boundaries of the austenite. This circumstance was employed here to mark out the size of the austenite grains. The piece of steel, which had been heated to a temperature of about 1675 degrees Fahr., and whose austenite grain size was sought, was placed for exactly 3 minutes in a furnace whose temperature was 1400 degrees Fahr.; at the end of the 3 minutes, at which time it had just about reached the temperature of the furnace, the piece was quenched in water. The structure is shown in Fig. 13. In the momentary slow cooling to 1400 degrees Fahr., some of the ferrite had precipitated in the grain boundaries, so that it now outlines the regions which had been individual grains of austenite, the remainder of each grain now being martensite (dark). It is seen that the grain size of the austenite indicated in this manner is quite like that suggested by the previous method, Fig. 12, namely, about size No. 6. The third and perhaps most convincing manner of indicating the austenite grain size was a new method developed by Miss M. Baeyertz. It consists in suitably water-quenching the specimen, and subsequently treating the polished section with a special picric acid stain. Fig. 14 shows one of her photographs of this same steel, the sample having been quenched from 1600 degrees Fahr. and treated with the aforementioned staining reagent. Its appearance confirms the estimate of austenite grain size suggested by the two previous methods.

The grain size remains unchanged even after a number of hours of heating at temperatures as high as 1675 degrees Fahr. Thus Figs. 15, 16 and 17 show the austenite grain size after 12 minutes, 1 hour and 4½ hours at 1675 degrees Fahr.

The grain size, as we have said, persists up to nearly 1700 degrees Fahr. At 1700 degrees Fahr. (in this particular steel) a change sets in. Fig. 18 shows the structure after heating for 8 hours at 1700 degrees Fahr. and quenching in oil. It is seen that some new large grains have formed, which grow by spreading across the small No. 6 grains which were present before. After 8 hours at 1700 degrees Fahr., perhaps 15 to 20 per cent of the total volume is occupied by these large grains. If the heating temperature (still in the absence of carburizing) is raised to 1800 degrees Fahr., the grain growth is much more rapid, so that 20 per cent of

the volume is occupied by the large grains after only 1½ hours, as indicated in Figs. 19 and 20. Fig. 19 is the usual oil quench and Fig. 20 shows the same grain size by the method of ferrite precipitation. If the heating at 1800 degrees Fahr. is continued up to 8 hours, the large grains will have continued to grow so that at the end of that time practically the whole structure consists of large (No. 1) grains.

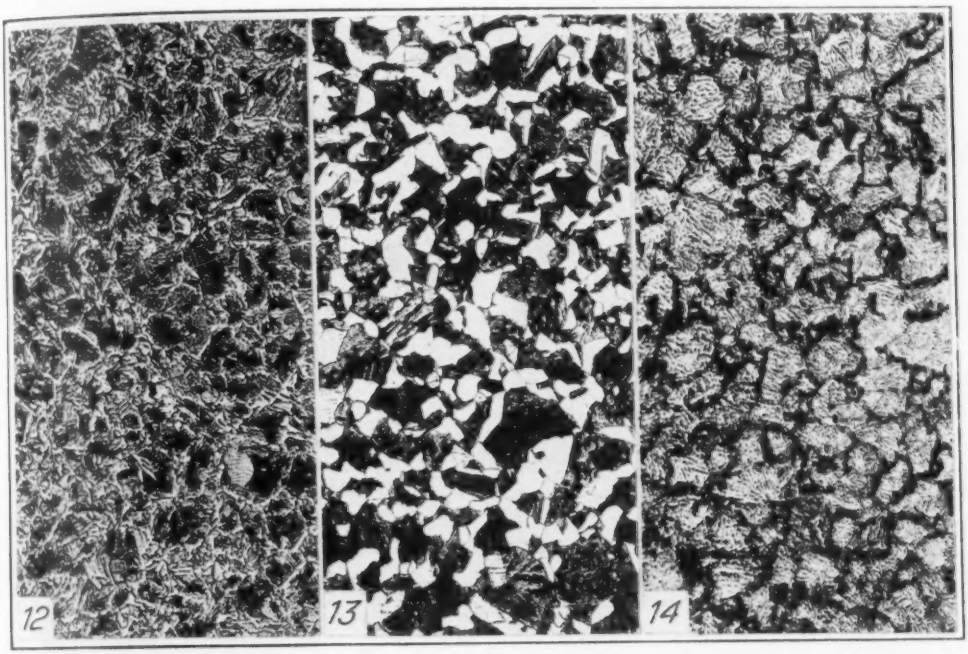
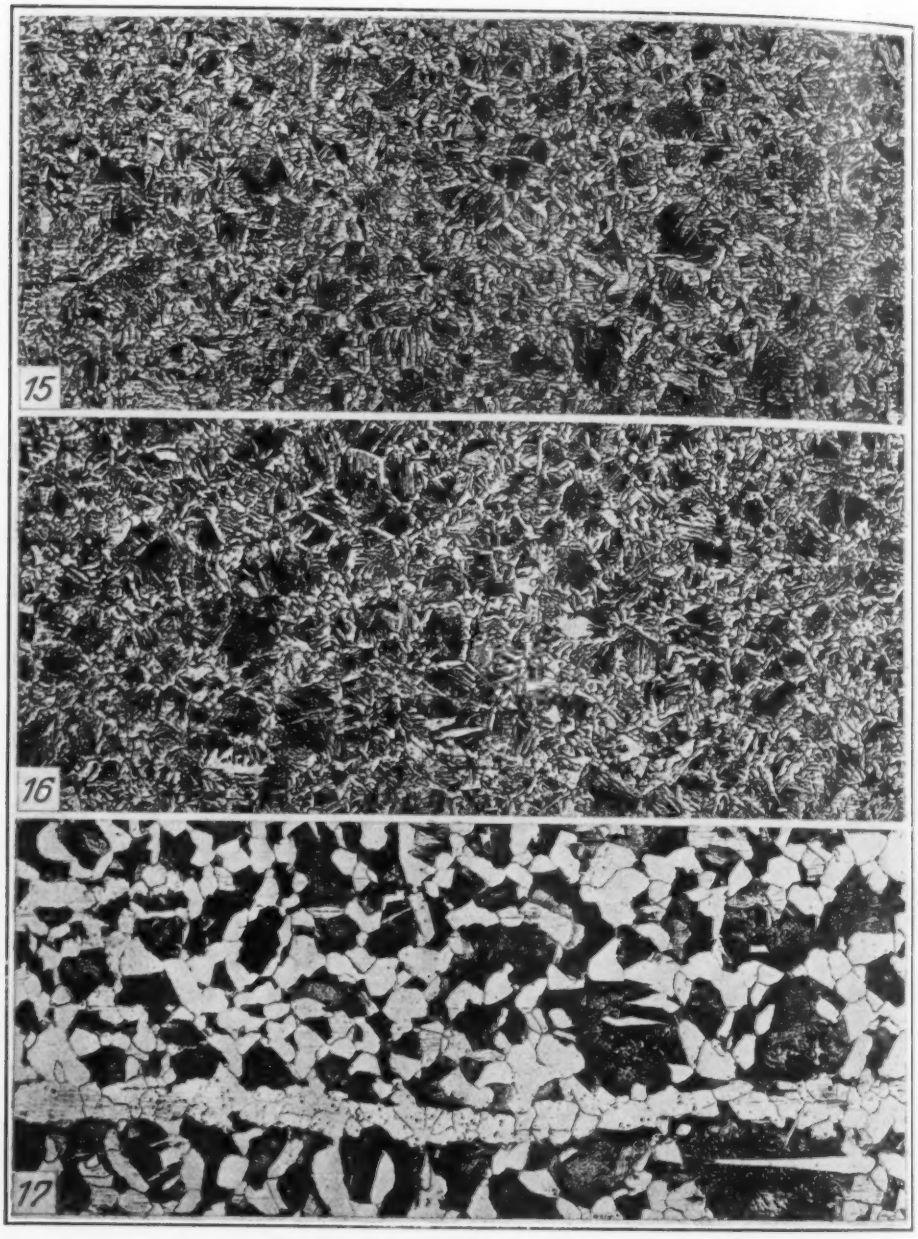


Fig. 12—Steel No. 1. Heated to 1580 Degrees Fahr. and Quenched in Oil. × 100.
Fig. 13—Steel No. 1. Heated to 1675 Degrees Fahr. and Quenched for Ferrite Precipitation. × 100.
Fig. 14—Steel No. 1. Heated to 1600 Degrees Fahr. and Quenched in Water. Special Picric Acid Stain. × 100.

Difference in Austenite Grain Size as Between Case and Core

To return now to Fig. 18. We see that about 20 per cent of the structure is coarse-grained and the remainder fine-grained. But if we compare this with Fig. 2, we see that in the *carburized* zone as much as 80 per cent is coarse and only 20 per cent is fine. This is a very marked disparity in grain size between the carburized zone and the uncarburized portion,—at this particular temperature, in this steel, the austenite grain size in the case is much larger than in the core.[4]

[4]In considering disparity between case and core, two phenomena must be considered,—the one described here and the one described by Bain, who showed that the formation of Al_2O_3 during carburizing may cause the case to be finer than the core.



Figs. 15, 16 and 17—Steel No. 1. Heated at 1675 Degrees for 12 Minutes, 1 Hour and 4½ Hours, Respectively, and Quenched.
Figs. 15 and 16, Quenched in Oil. Fig. 17, Ferrite Precipitation.

We must therefore examine the development of grain size of the steel as carburized at different temperatures. At low temperatures, such as 1600 degrees Fahr., the grain size as carburized is the same as without carburizing. Figs. 21 and 22 show the austen-

ite grain size of core and case when carburized for 4 hours at 1600 degrees Fahr. The grain size in the two is alike and is the same No. 6 as obtained in the uncarburized steel as soon as it was heated above the transformation range. When the carburizing temperature is raised to 1650 degrees Fahr., however, coarse grains begin to develop in the carburized portion, so that at the end of 8 hours the

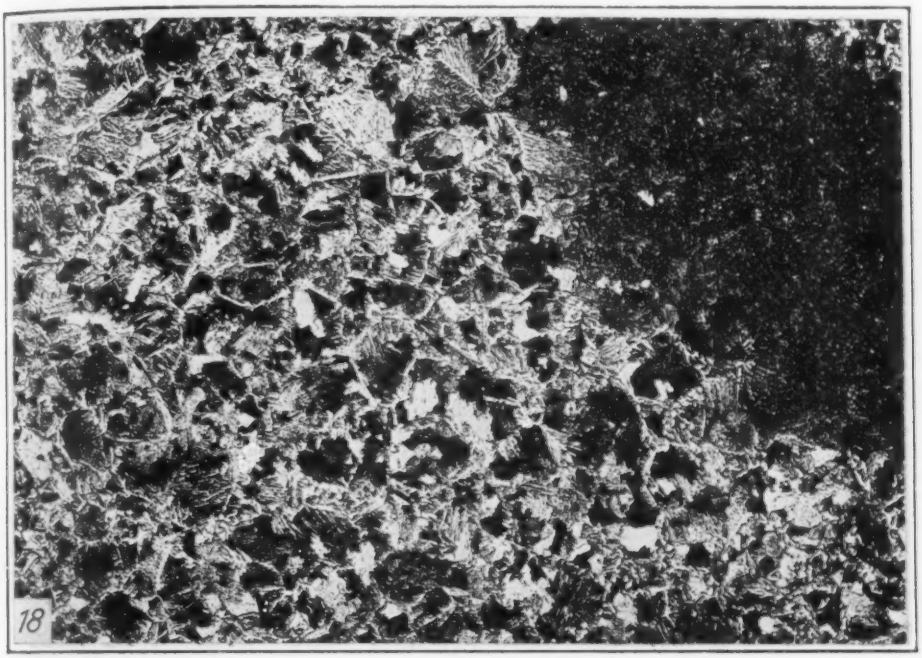
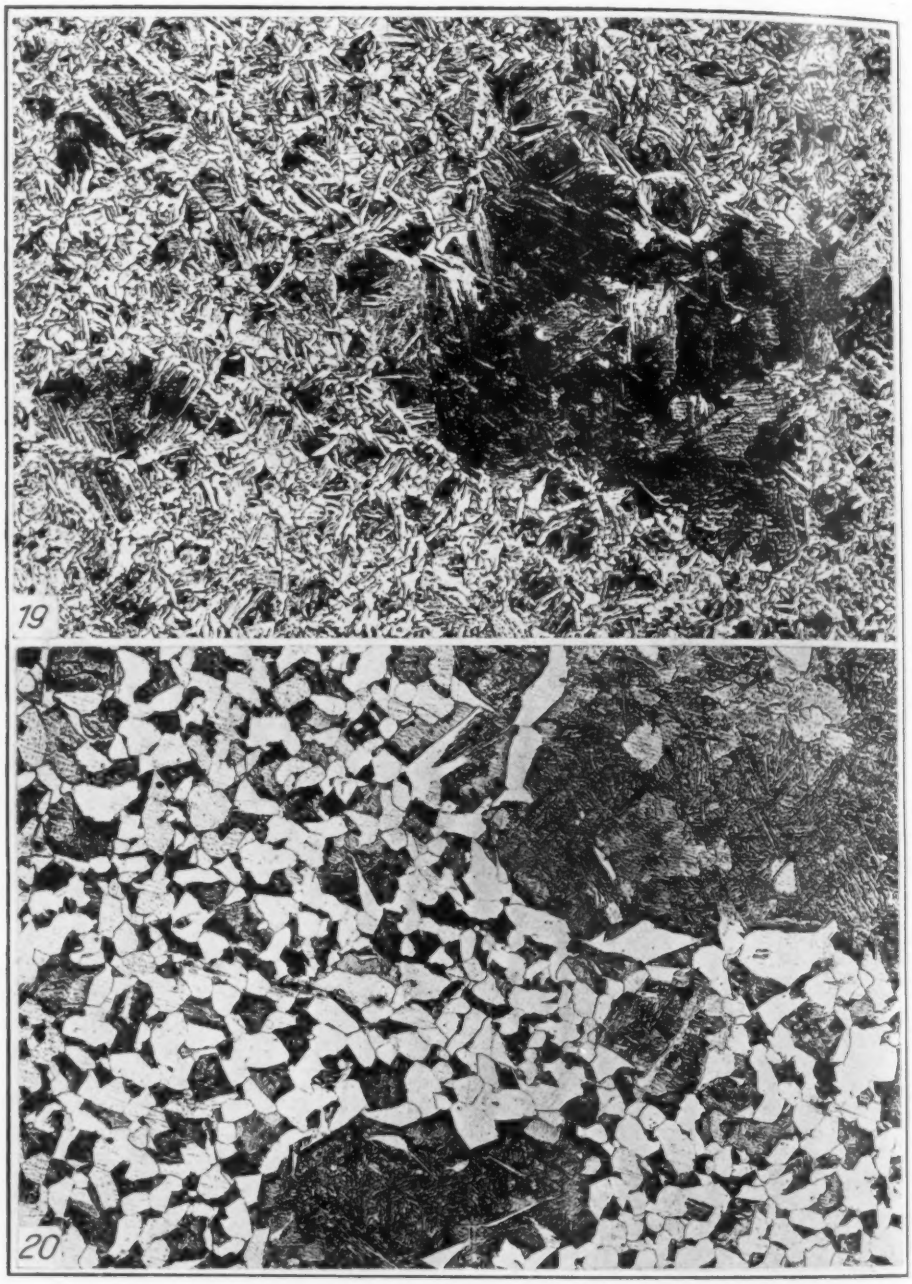


Fig. 18—Steel No. 1. Heated 8 Hours at 1700 Degrees Fahr. and Quenched in Oil. × 100.

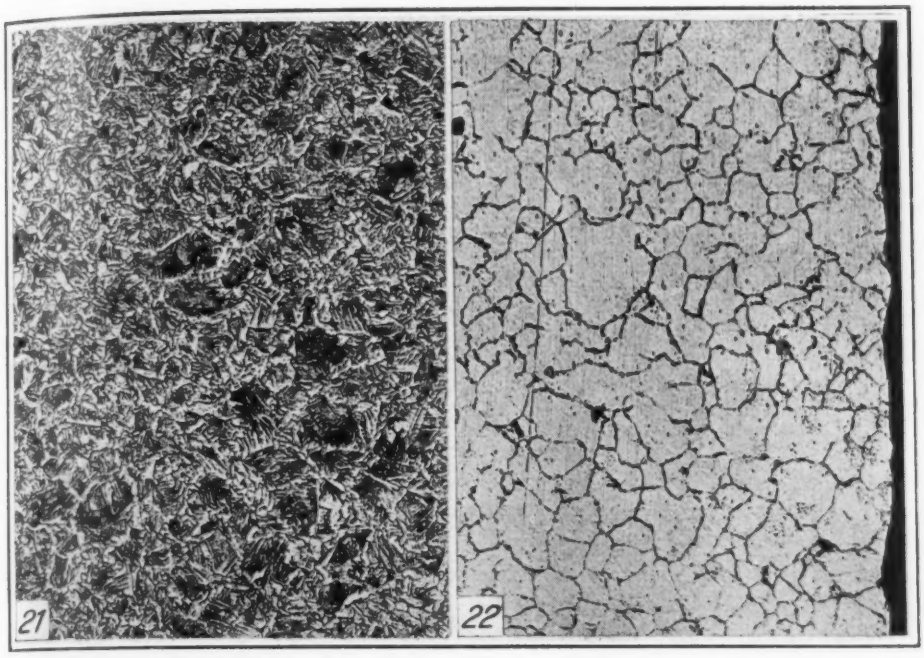
structure contains about 15 per cent of coarse grains. If the carburizing temperature is raised to 1675 degrees Fahr. the rate of growth increases, so that at the end of 8 hours the carburized zone is about half coarse grains, the remainder being still the original No. 6 size. It will be recalled that at this temperature the uncarburized steel still consisted wholly of fine grains—no coarsening had as yet begun in the absence of carburizing. As the carburizing temperature is raised, the rate of coarsening increases, so that after 8 hours at 1725 degrees Fahr., the carburized zone consists almost wholly of No. 1 grains.

The coarsening in the case as compared with the core may therefore be represented in a diagram, as in Fig. 23. The ordinates are the percentage of the total volume occupied by the coarsened



Figs. 19 and 20—Steel No. 1. Heated 1½ Hours at 1800 Degrees Fahr. and Quenched. Fig. 19, Quenched in Oil. Fig. 20, Ferrite Precipitation. × 100.

grains, after 8 hours at the temperatures indicated in the abscissae. It is seen that formation of coarse grains in the carburized portions occurs at temperatures at least 50 degrees Fahr. lower than in the uncarburized portions.



Figs. 21 and 22—Core and Case in Steel No. 1. Treated at 1600 Degrees Fahr. Fig. 21, Heated 4 Hours (without carburizing) and Quenched in Oil. × 100. Fig. 22, Carburized 4 Hours, Hypereutectoid Zone (sodium picrate etch). × 100.

Grain Size of Various Plain Carbon Steels

Aside from the above disparity between case and core, we have seen that steel No. 1 may be adjudged to be No. 6 or No. 1 grain size (by the McQuaid-Ehn test) depending on whether the carburizing was carried out below or above the coarsening temperature. Obviously, this leads to speculation in regard to the general behavior of plain carbon steels, of which Steel No. 1 gave one manifestation.

A group of eight steels (including Steel No. 1) were therefore carburized at a series of temperatures. The compositions of the steels are given in Table I. The (austenite) grain sizes as judged from the carburized zones, after carburizing at the various temperatures, are also given in Table I. The carburizing time was in all cases 8 hours.

It will be observed that three of the steels were coarsened at 1700 degrees Fahr., the remainder being fine-grained. At higher temperatures, these three steels were of course likewise coarsened. A fourth steel began to coarsen at 1800 degrees Fahr., and was completely coarsened at 2000 degrees Fahr. A fifth steel showed signs

of incipient coarsening at 2000 degrees Fahr. The remaining three steels were still fine-grained at 2000 degrees Fahr., the grain size being precisely the same after 8 hours at 2000 degrees Fahr. as after the same length of time at 1700 degrees Fahr. One is led

Table I

Grain Size of Low Carbon Steels After Carburization

Steel No.	Chemical Composition					Grain Size After 8 Hr. Carburizing			
	C	Mn	P	S	Si	1700°F.	1800°F.	1900°F.	2000°F.
1	0.15	0.44	0.015	0.019	0.22	85% No. 1 15% No. 6	No. 1	No. 1	No. 1
2	0.15	0.46	0.015	0.017	0.16	No. 1	No. 1	No. 1	No. 1
3	0.12	0.37	0.011	0.025	..	No. 6	30% No. 1 70% No. 6	85% No. 1 15% No. 6	No. 1
4	0.14	0.79	0.011	0.017	0.28	No. 6 to No. 7	No. 6 to No. 7	No. 6	No. 6
5	0.17	0.79	0.009	0.014	0.29	No. 5 to No. 6	No. 5 to No. 6	No. 6	No. 6
6	0.14	0.80	0.008	0.016	0.22	No. 6	No. 6	No. 5 to No. 6	No. 6
7	0.15	0.38	0.011	0.017	0.21	No. 1	No. 1	No. 1	No. 1
8	0.18	0.78	0.010	0.018	0.24	No. 6 to No. 7	No. 6 to No. 7	No. 6	No. 5 to No. 6 with few No. 1

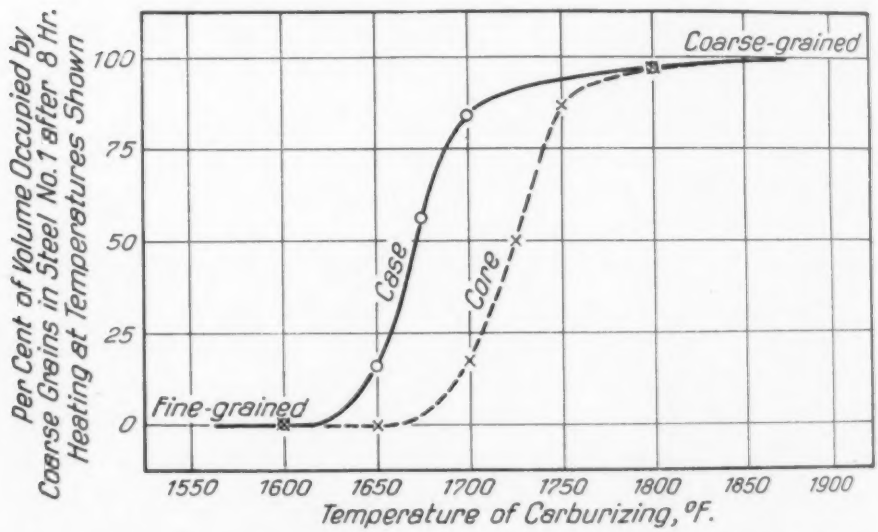
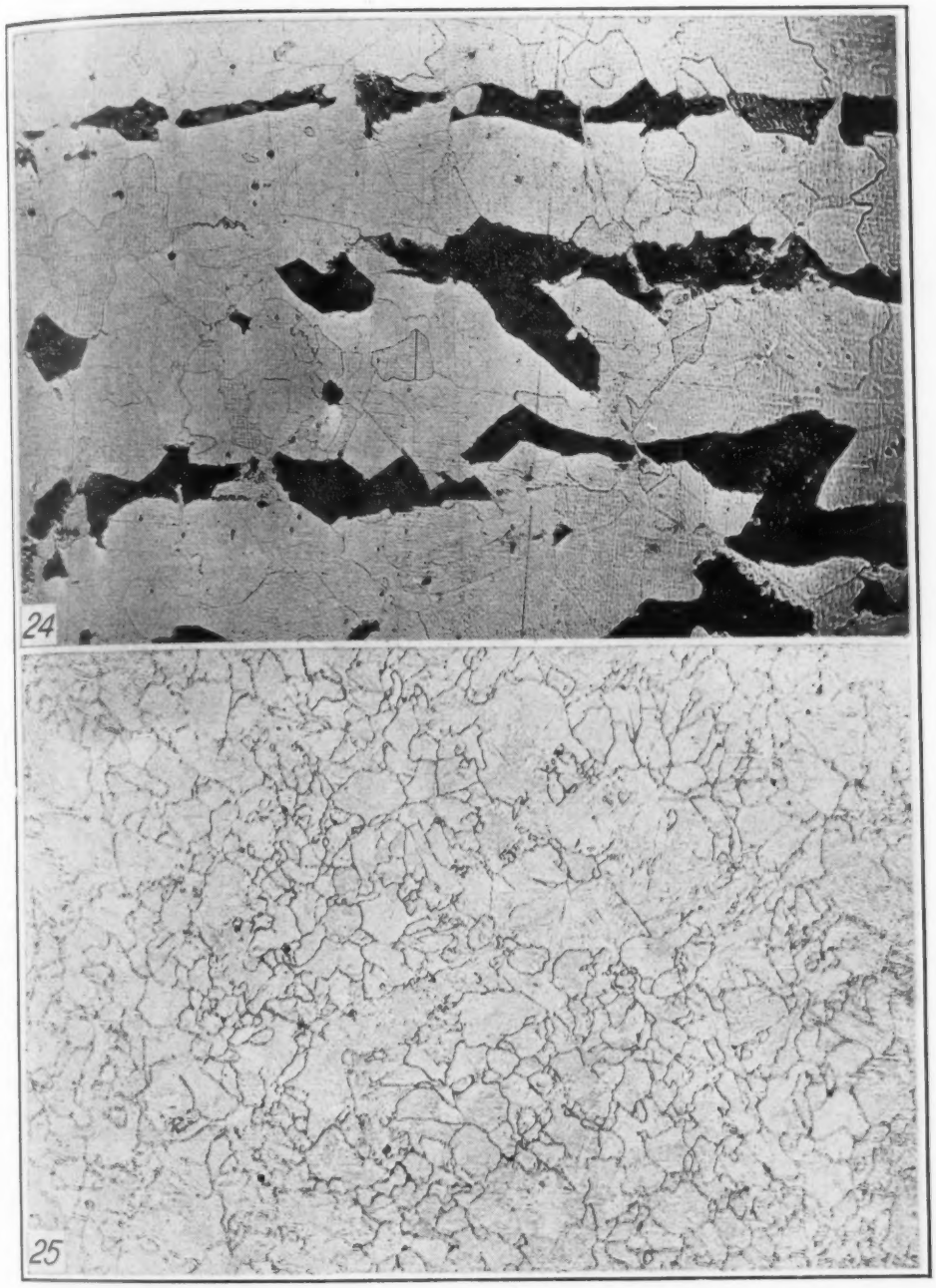


Fig. 23—Extent of Coarsening in Case and Core of Steel No. 1 when Carburized at Different Temperatures.

to the important conclusion, then, that at temperatures at which coarsening (exaggerated grain growth) takes place, the time and temperature of carburizing affect the results; but in the temperature range where exaggerated grain growth fails to take place (which not infrequently extends up to 2000 degrees Fahr.), the steel may



Figs. 24 and 25—Steel No. 9. Fig. 24, As-received. Fig. 25, Carburized 8 Hours at 1700 Degrees Fahr., Hypereutectoid Zone (sodium picrate etch). × 100.

be carburized at any temperature and for any length of time, and the grain size will remain precisely the same, namely, at the size formed when the steel first transformed to austenite upon heating.

Effect of Heat Treatment on Grain Size

We have seen in the above examples that, during the heating up to the carburizing temperature, a steel transforms to austenite of a certain (small) grain size, and that it maintains this grain size for an indefinite length of time at any temperature up to the temperature at which exaggerated grain growth sets in. We have not yet, however, studied any factors which affect this initial austenite grain size.

Consider an instance of carburization where no exaggerated grain growth took place, that is, a steel which when carburized at

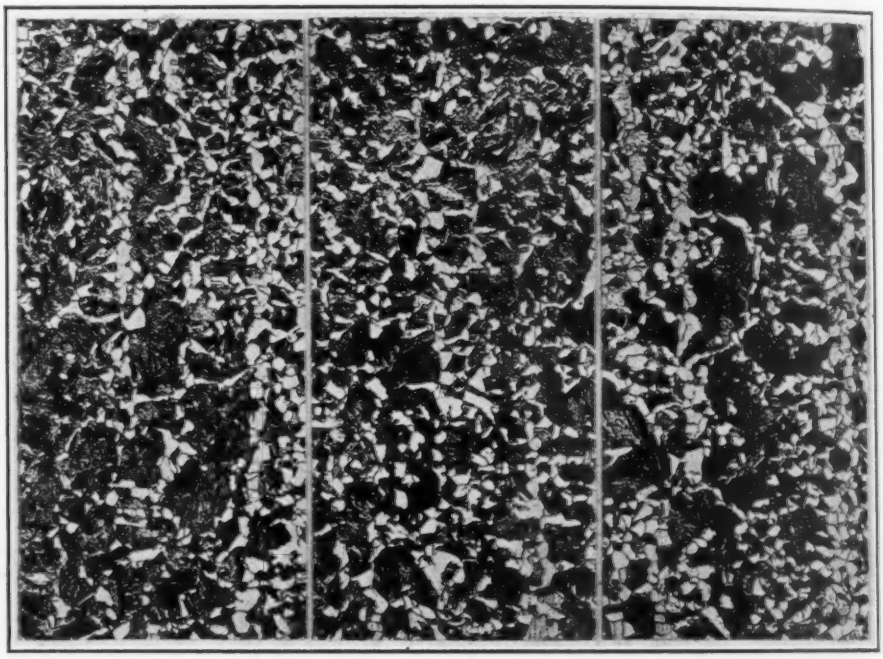
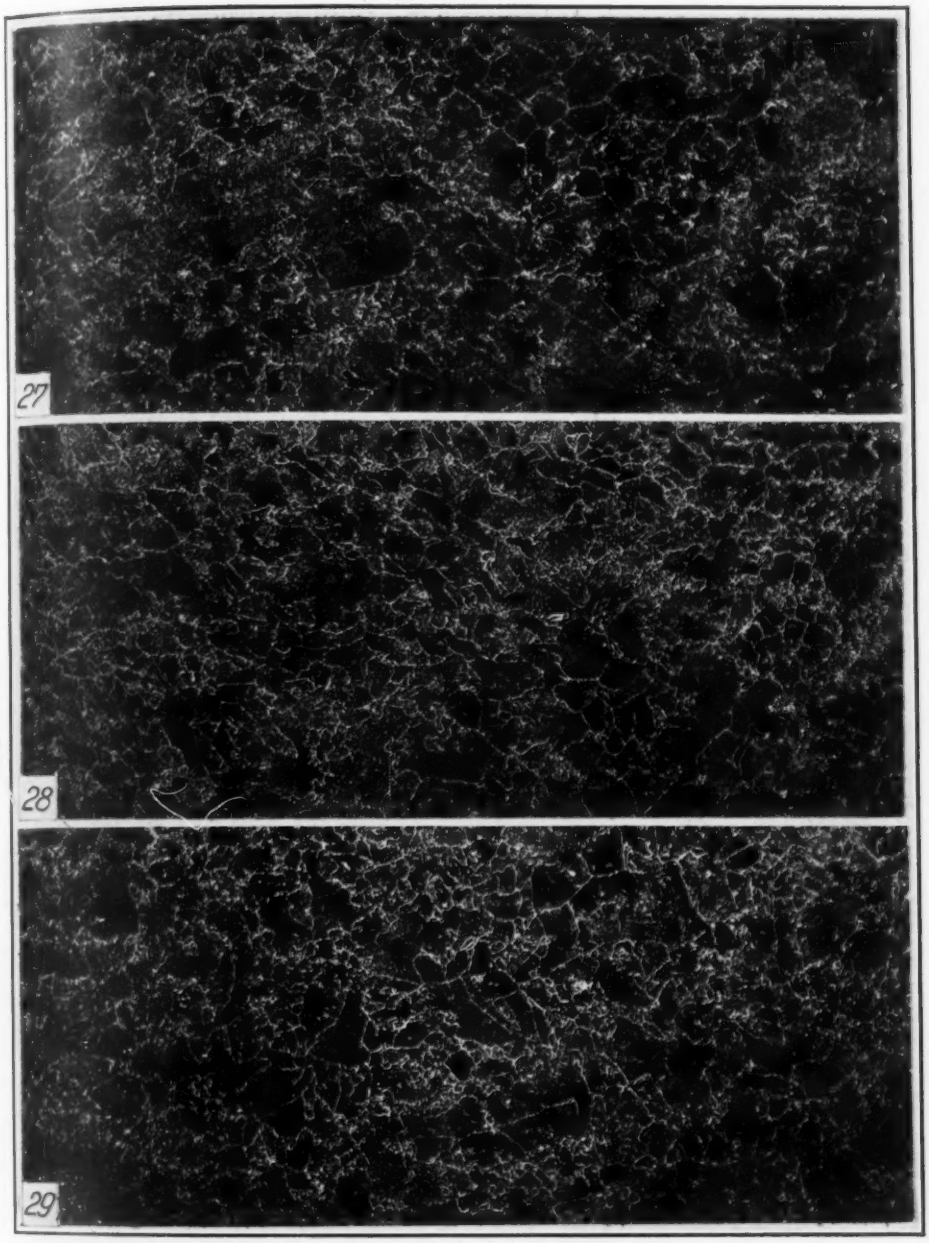


Fig. 26—Steel No. 9. Heated to 1700 Degrees Fahr., Held 1 Hour, Cooled for Ferrite Precipitation and Quenched. × 100. (Because of the banding, the steel was cooled on a gradient to precipitate ferrite in the different bands before quenching. Hence the composite picture.)

1700 degrees Fahr. behaved as did plain carbon steel No. 1 when carburized at 1600 degrees Fahr. An instructive example was found in a heat of nickel-molybdenum steel (Steel No. 9) of the following composition:—

Carbon	Mang.	Phos.	Sulphur	Silicon	Nickel	Molyb.	Chromium
0.17	0.51	0.007	0.004	0.22	1.68	0.23	0.07

The steel was in the form of 5 by 5-inch billet rolled from a 21-inch diameter ingot. The steel before carburizing had the struc-



Figs. 27, 28 and 29—Steel No. 9. Carburized at 1700 Degrees Fahr. for 1 Hour, 3 Hours and 6 Hours, Respectively. Hypereutectoid Zone. × 100.

ture of Fig. 24, and when given a McQuaid-Ehn test showed a grain size in the hypereutectoid zone of about No. 5, as shown in Fig. 25 (sodium picrate etch).

If this steel is heated to 1700 degrees Fahr. without carburizing, the austenite grain size may in this case likewise be determined

by the method of ferrite precipitation, as outlined above. The structure obtained is shown in Fig. 26, and is seen to exhibit a grain size of about No. 5. We find here then a case similar to the 1600 degrees Fahr. carburizing of steel No. 1, in that the austenite of the case has the same grain size as the austenite of the core. It may again be noted that the grain size was established at the beginning of the carburizing period, and was maintained substantially constant during the whole of the heating at 1700 degrees Fahr.

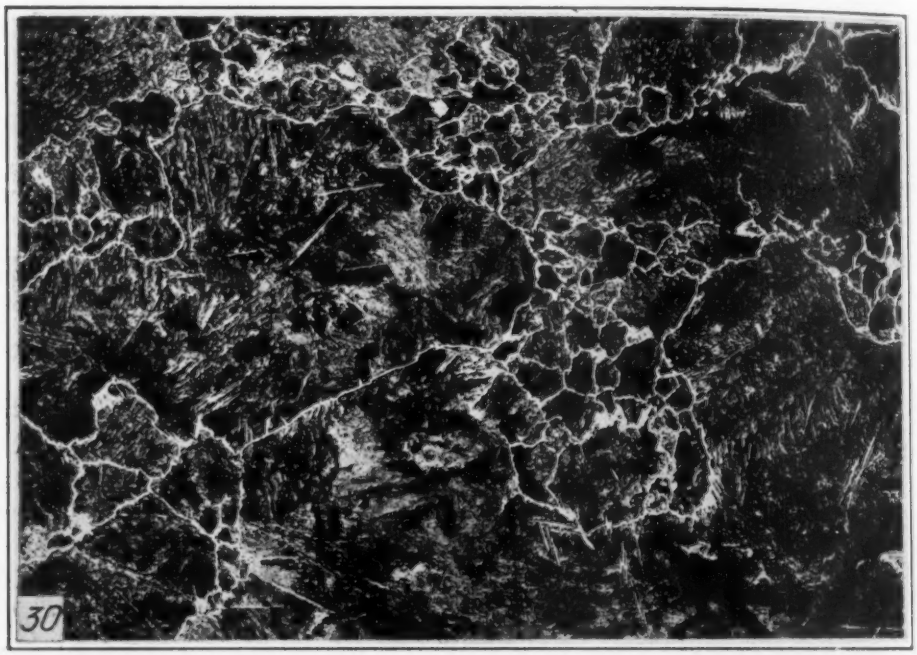


Fig. 30—Steel No. 9. Carburized 8 Hours at 2150 Degrees Fahr. Hypereutectoid Zone. × 100.

Figs. 27, 28 and 29 show the hypereutectoid grain size after carburizing for 1 hour, 3 hours and 6 hours respectively. It is evident that the grain size established in the core determines the grain size in the carburized region.

This steel No. 9 was likewise explored to discover the temperature at which exaggerated grain growth took place. At 1900 and at 2100 degrees Fahr. it still displayed grain size No. 5, as in Fig. 25, but at 2150 degrees Fahr. it underwent substantial coarsening, as shown in Fig. 30.

Now as to the initial austenite grain size. Reference has already been made to the fact that McQuaid-Ehn grain size is often independent of prior heat treatment, but that there are exceptions

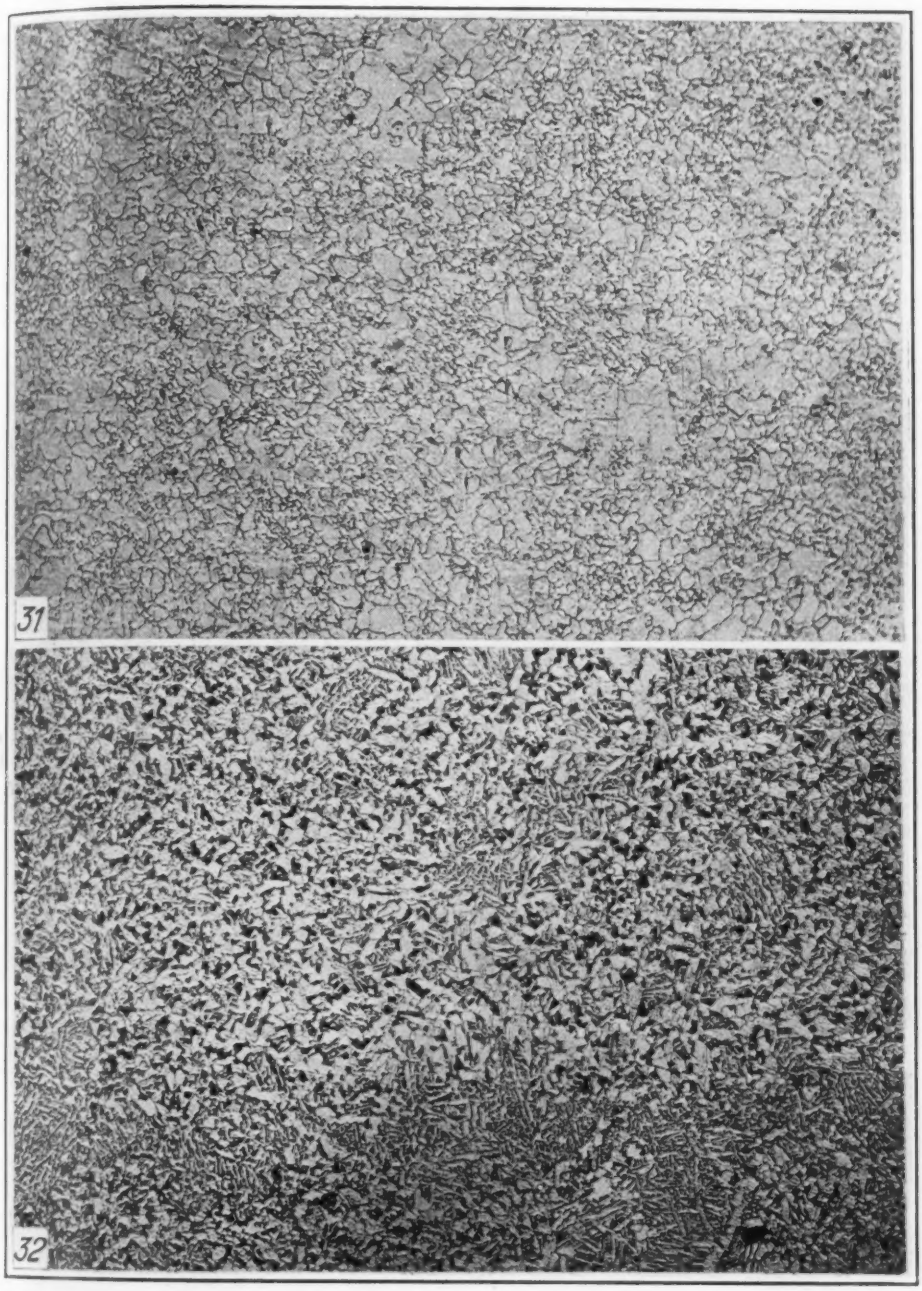


Fig. 31—Steel No. 9. Heated to 1600 Degrees Fahr. and Cooled in Air, then Carburized 8 Hours at 1700 Degrees Fahr. Fig. 32, The Same, Before the Carburizing. X 100.

to this behavior. Steel No. 9 is one of these exceptions. The circumstance which led to the present inquiry was the observation that the McQuaid-Ehn grain size of this steel after normalizing was

smaller than was obtained if the normalizing was omitted. If the piece of steel No. 9 was heated to 1600 degrees Fahr. and cooled in air, before carburizing, the subsequent McQuaid-Ehn grain size after carburizing was as shown in Fig. 31, (sodium picrate etch), i. e., about No. 9. This compares with size No. 5, already shown in Fig. 25, when the steel from the slowly cooled billet was carburized directly (without intervening heat treatment).

In seeking a cause for this behavior, it was edifying to compare the structures which existed in the pieces before carburizing. The structure of the normalized piece (prior to carburizing) is shown in Fig. 32, and it is quite striking that the ferrite grains are small when compared with the sample which was not normalized, Fig. 24. That is, the steel with the smaller ferrite grains before carburizing gave the smaller subsequent McQuaid-Ehn grain size. An obvious next step was to ascertain if there was any regularity in this relationship. For this it would be necessary to prepare the steel so that samples would have a series of different ferrite grain sizes, and then examine the McQuaid-Ehn grain sizes when these samples had been carburized. The series of ferrite grain sizes was obtained by heating samples from the original billet as follows:

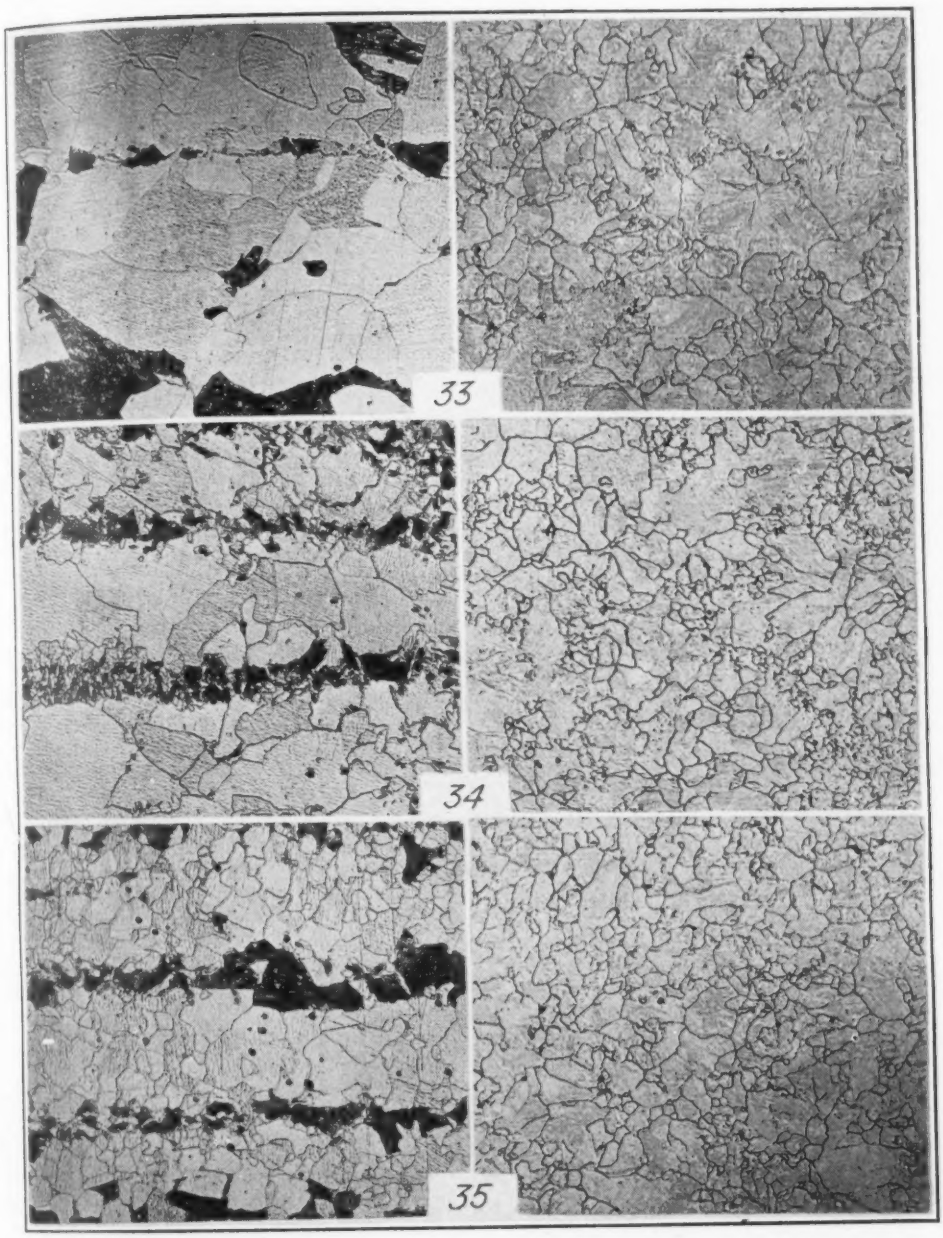
16-N	Heated to 1600 degrees Fahr. and cooled in air.
17-1	Heated to 1700 degrees Fahr. and cooled in air.
17-2	Heated to 1700 degrees Fahr., cooled in 3-inch box in air.
17-3	Heated to 1700 degrees Fahr., normal furnace cooling.
17-4	Heated to 1700 degrees Fahr., delayed furnace cooling.
19	Heated to 1900 degrees Fahr., cooled with furnace.
21	Heated to 2100 degrees Fahr., cooled with furnace.
23	Heated to 2300 degrees Fahr., cooled with furnace.
15	Heated to within critical range, cooled in air.
1	Original billet.

These pieces were thereupon carburized, and when the samples were then placed in the order of decreasing McQuaid-Ehn grain size, they were found to be arranged as follows:

1, 15, 23, 21, 17-4, 19, 17-3, 17-2, 17-1, 16-N.

This was almost precisely in the order of decreasing ferrite grain size before carburizing, as will be seen by examining Figs. 33 to 41.[5] At the left in each case is the structure before carburizing, and at the right is the structure in the hypereutectoid zone after carburizing. It will be observed that as the prior ferrite grain size changed

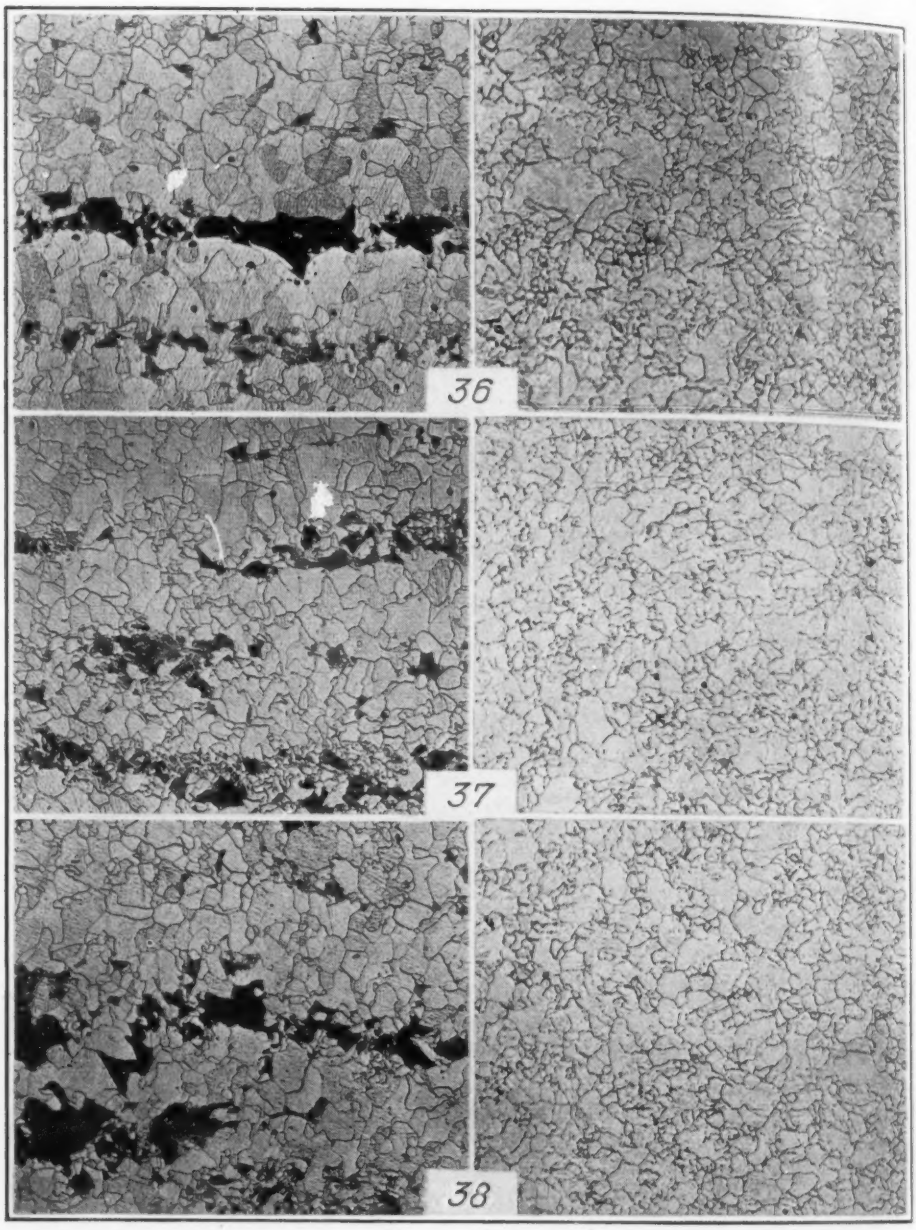
[5]H. C. T. Han showed that when the hypereutectoid grains are small, the grain size is observed much more clearly if the etching is done with sodium picrate, and the photographs are his.



Figs. 33, 34 and 35—Steel No. 9. Uncarburized and Carburized. The Samples had the Following Treatments Prior to Carburizing: Fig. 33, No Treatment; Fig. 34, Heated to Within the Critical Range; Fig. 35, Heated to 2300 Degrees Fahr. × 100.

from No. 4 to No. 8, the subsequent McQuaid-Ehn grain size changed from No. 5 to No. 9.

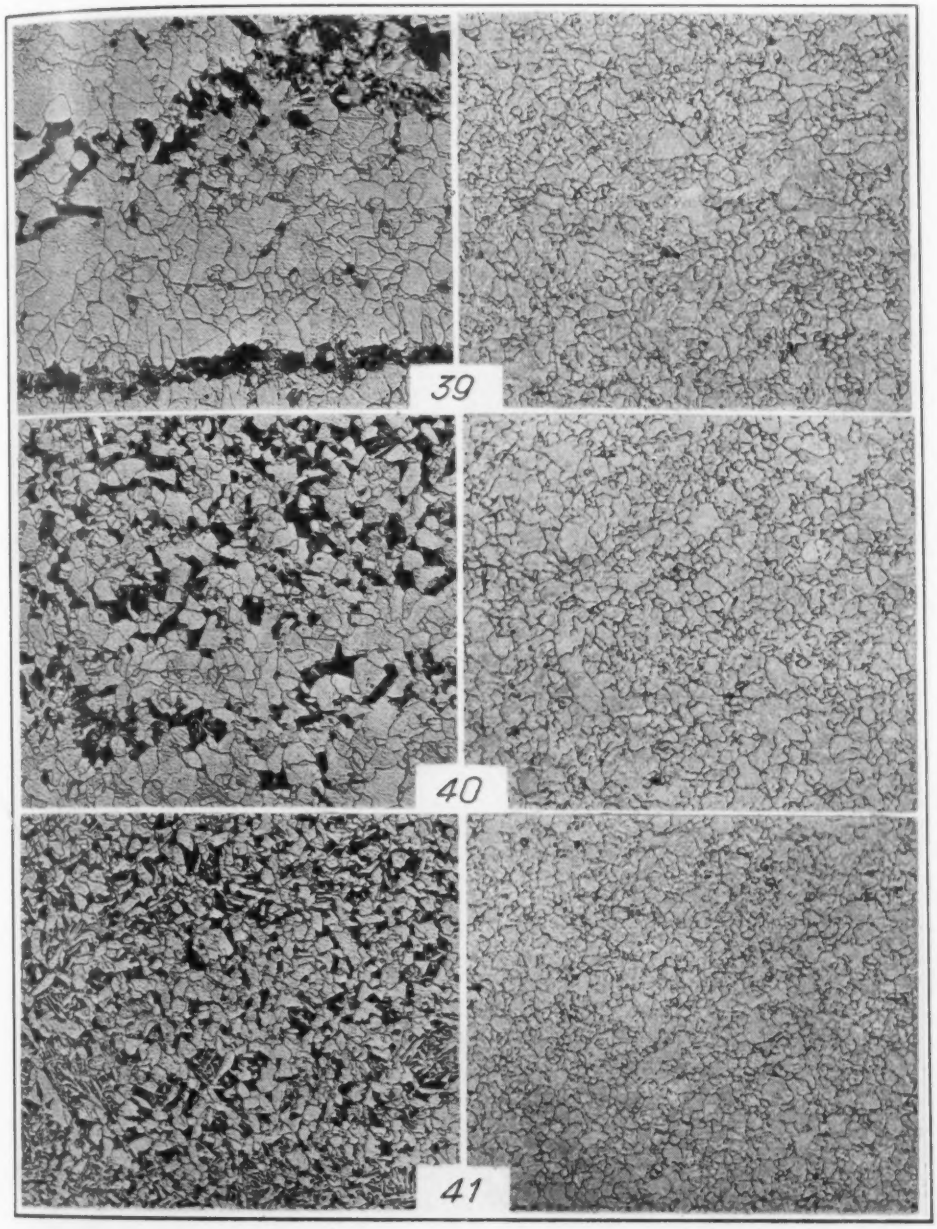
One seems warranted in concluding, therefore, that in some steels the McQuaid-Ehn grain size is influenced by any prior heat



Figs. 36, 37 and 38—Steel No. 9. Uncarburized and Carburized. The Samples had the Following Treatments Prior to Carburizing: Fig. 36, Heated to 2100 Degrees Fahr.; Fig. 37 Heated to 1700 Degrees Fahr. and Cooled 100 Degrees Fahr. per Hour; Fig. 38, Heated to 1900 Degrees Fahr. × 100.

treatment which changes the ferrite grain size. And, at the same time, this suggests a reason why cold work sometimes leads to a finer McQuaid-Ehn grain size; obviously, it may break up larger ferrite grains and lead to a smaller initial ferrite grain size.

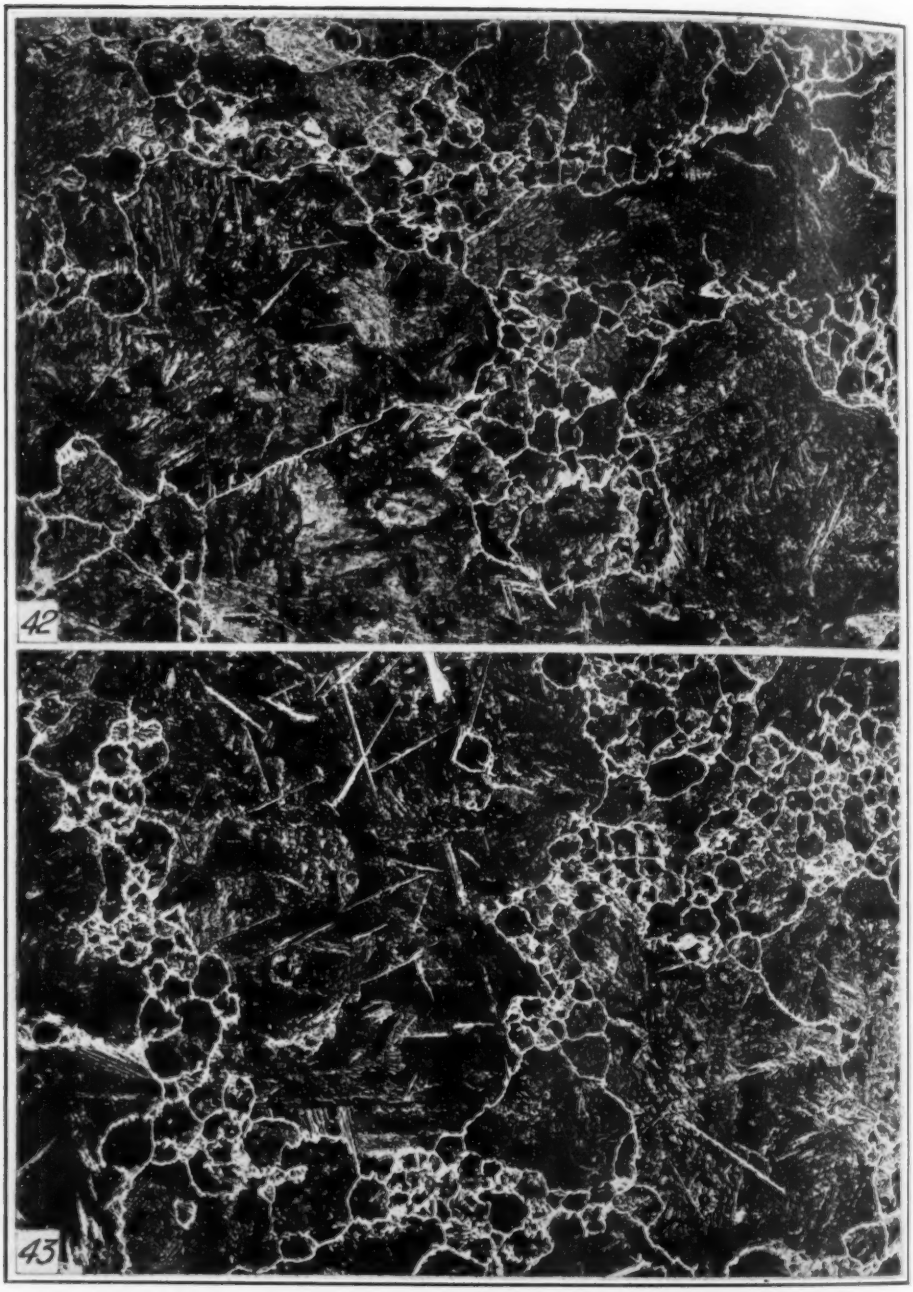
Attention may now again be directed to the fact that this rela-



Figs. 39, 40 and 41—Steel No. 9. Uncarburized and Carburized. The Samples had the Following Treatments Prior to Carburizing: Fig. 39, Heated to 1700 Degrees Fahr. and Cooled 250 Degrees Fahr. per Hour; Fig. 40, Heated to 1700 Degrees Fahr. and Cooled in Air; Fig. 41, Heated to 1600 Degrees Fahr. and Cooled in Air.

tionship (between prior ferrite and subsequent austenite) exists here in the absence of exaggerated grain growth. One may well ask what happens when exaggerated grain growth takes place. Hence it is appropriate to record an early experiment by L. Schapiro,[6] who

[6]Hitherto unpublished.



Figs. 42 and 43—Steel No. 9. Carburized 8 Hours at 2150 Degrees Fahr. Fig. 42, No Treatment Before Carburizing. Fig. 43, Heated to 1600 Degrees Fahr. and Cooled in Air Before Carburizing. × 100.

was seeking an answer to this same question. He carburized samples of this same steel No. 9 at 2150 degrees Fahr. for 8 hours. One sample was original billet, having the structure of Fig. 24, and

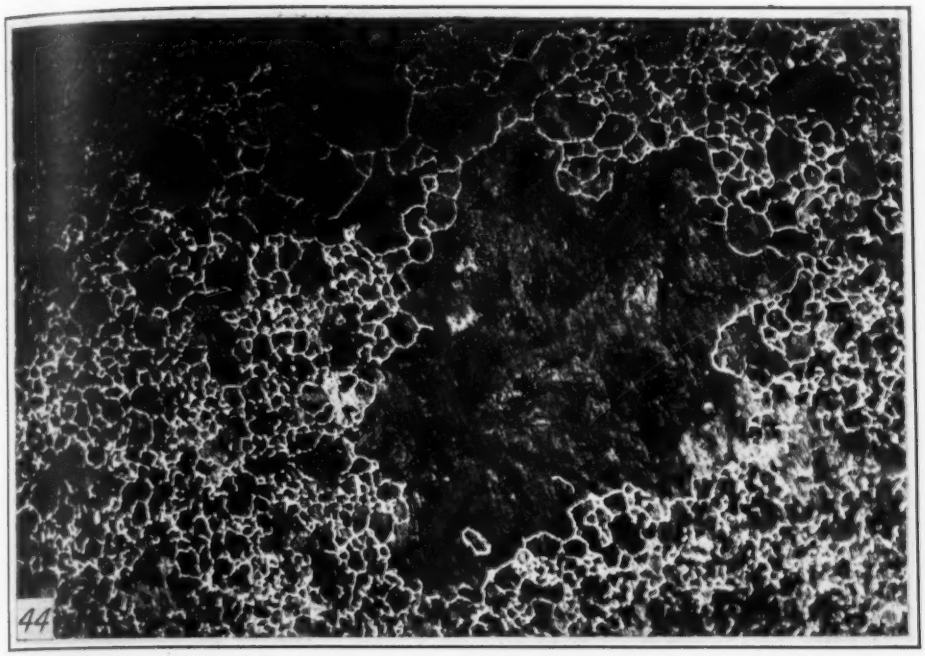


Fig. 44—Steel No. 10. (Carbon 0.40, Manganese 0.72, Silicon 0.21, Nickel 1.18, Chromium 0.59 Per Cent) Carburized 8 Hours at 1700 Degrees Fahr. × 100.

the other had been normalized, its structure being as in Fig. 32. The 2150 degrees Fahr. carburizing resulted in the structures of Figs. 42 and 43. It is evident that exaggerated grain growth has taken place in both samples, resulting, in both cases, in a preponderance of No. 1 grains, with a few of the smaller grains still unabsorbed. And this, of course, raises a question which is yet to be answered: Are the steels whose McQuaid-Ehn grain size is independent of prior treatment, the ones in which exaggerated grain growth takes place in carburizing at 1700 degrees Fahr.?

Mixed Grain Size

In some steels, such as Steel No. 1 above, practically complete coarsening takes place in 8 hours at 1700 degrees Fahr., so that the grains exhibit substantially a uniform No. 1 size. In other steels, such as Steel No. 9, no coarsening whatever takes place at 1700 degrees Fahr., and a McQuaid-Ehn test results in a uniform fine grain size. But there are some steels for which 1700 degrees Fahr. is apparently just the temperature at which exaggerated grain growth begins. In such steels, grains begin to grow at isolated regions throughout the steel, and continue to grow but slowly during the

whole course of the 8-hour carburizing period. The result is a structure which has sometimes been termed "mixed grain size," as illustrated in Fig. 44. The latter is from a carburized sample of chromium-nickel steel, of approximately S.A.E. 3135 composition. Fig. 44 is distinctly reminiscent of Fig. 18, and the relationship is quite evident. The growth proceeds slowly, hence when the steel of Fig. 44 has been carburized at 1700 degrees Fahr. for only one hour, the exaggerated grains are still rather small. On the other hand, if the heating is continued beyond 8 hours, the grains continue to grow, eventually covering the whole piece. This steel, then, if it were carburized at 1700 degrees Fahr. for one hour, would exhibit a grain size of about No. 6 or No. 7, and if the carburizing were continued up to say 20 hours, the grain size would be No. 1.

Conclusions

In a carburizing test (McQuaid-Ehn test) for austenite grain size, the steel initially (during the heating-up in the carburizing pot) undergoes its transformation to austenite and in so doing comes to a certain (small) austenite grain size, usually in the range from No. 5 to No. 8.

The temperature of the piece, of course, continues to rise thereafter, up to the carburizing temperature. Every steel has a coarsening temperature which, if exceeded, causes coarse grains (No. 1 to No. 2) to form. If the carburizing temperature is above the coarsening temperature, the final carburized piece will consist partly or wholly of coarse grains. But if the carburizing temperature is at any temperature below the coarsening temperature (and the latter may be high, even above 2000 or 2100 degrees Fahr.) then the austenite grain size will remain unchanged, precisely what it was when the steel first transformed to austenite upon heating.

In some steels this initial austenite grain size is related to prior ferrite grain size and is in these cases affected by prior heat treatment.

Acknowledgments

It is with genuine pleasure and a certain humility that the author acknowledges the stimulating discussions of this subject, with his associates at the Illinois Steel Company. Special thanks are due also to Mr. Walther Mathesius, both for strict criticism and for generous encouragement.

DISCUSSION

Written Discussion: By Samuel Epstein, metallurgist, Battelle Memorial Institute, Columbus, Ohio.

Metallographers who examine both the case and core in making the McQuaid-Ehn test have noticed that a fine-grained case after carburizing is usually accompanied by a fine-grained core. Dr. Grossmann has strikingly demonstrated that the reason for this must be that during carburizing the austenite grains grow to about the same size in the high carbon case as in the low carbon core. The grain growth here is apparently largely independent of the carbon content. Thus the advantage of carburizing (over merely heating for a similar time to a similar temperature) in determining the grain growth characteristics of a steel, is only that after carburizing the grain size can be more readily recognized by the outlines of the cementite grain boundary network.

Structural steel in the as-rolled condition ordinarily does not indicate whether it is of the coarse or fine-grained type, i. e., in the as-rolled condition both types have about the same grain size. The explanation probably is that the usual rolling temperature is high enough to develop an equally coarse grain in both types of steel. The grain size may be reduced during the rolling, but both the coarse and fine-grained types end up with about the same medium sized grain.

In this connection Dr. Grossmann's observation that some of his fine-grained steels showed no grain growth even after carburizing at so high a temperature as 2100 degrees Fahr. is of decided interest. It would indicate that if the heating temperature for rolling such a fine-grained type of steel were kept within this range (possibly this temperature could even be somewhat higher, for according to the data in this paper, the temperature at which coarse grain resulted on heating alone was about 50 degrees Fahr. higher than on carburizing) the steel would not become coarse-grained on heating for rolling and would consequently be fine-grained directly after rolling. Such a steel would, therefore, have the fine grain and the accompanying properties of fine grain, which are now only obtainable by normalizing.

Indeed, the coarse-grained type of steel may not become sufficiently fine-grained in the sense of showing the properties of the fine-grained type of steels, even after normalizing, although these properties might perhaps be approximated if the normalizing temperature were held very closely above the critical temperature—more closely, probably, than would be commercially practicable.

The characteristic properties of the fine-grained steels, as tested after normalizing, are high yield point, high impact resistance, and low susceptibility to embrittlement after cold work. The last property, which has been termed "non-aging," has only been studied recently, but the fact that the core of the fine-grained steels after carburizing shows much better impact resistance than the core of the coarse-grained steels after carburizing has been known for some time.

In regard to the manner in which the different grain sizes arise, Grossmann has shown that the grain size on carburizing at 1700 degrees Fahr. is influenced somewhat by the grain size of the steel before carburizing. While

this is of undoubted interest in respect to the general laws of recrystallization and grain growth in iron and steel on heating through the critical range, it does not appear to get at the root of the cause of fine and coarse-grained steels. Thus, if a very coarse-grained type of steel had been chosen for these experiments, such as the one designated No. 2, the relation between grain size before and after carburizing would not have been revealed, at least not for the same carburizing temperature of 1700 degrees Fahr. It would seem that the part played by the grain size of the steel before carburizing in causing coarseness or fineness of grain is almost as much a secondary or minor matter as the part played by cold work, which is mentioned and which is obviously of minor consequence.

There is now hardly any question that the principal cause of the coarse and fine-grained types of steels is the presence of finely divided refractory particles which may act as nuclei for solidification and recrystallization and as obstructants to grain growth. Finely divided alumina in the steel is probably the most usual cause of fine grain. Various steel manufacturers have claimed they can control the grain size characteristics of their steel. This must be accomplished by the proper use of aluminum or similar drastic deoxidizer, resulting in the formation of refractory particles insoluble in the steel and hence unable to coalesce in the range of carburizing temperatures or higher.

The control of the behavior of such deoxidizers should result in control of the whole class of phenomena associated with the terms "body" and "aging" in steel. That such control may produce some worth while results is attested by the properties of Izett steel, which is a fine-grained type of steel, containing about 0.05 per cent aluminum, but which is yet relatively free of large alumina inclusions or segregates. This opens up a very large subject but the above is sufficient to emphasize that in discussing "the manner in which grain sizes arise, and in particular, the influences which cause them to vary" the all important factor of the presence of finely dispersed inclusions cannot be omitted.

As a minor correction, it should be stated that etching with picric acid to reveal the grain boundaries in martensitic steel is not new, as this procedure was described a good many years ago by Archer.

Written Discussion: By E. C. Bain, Research Laboratory, U. S. Steel Corporation, Kearny, New Jersey.

I would like to call attention to the value of Dr. Grossmann's picture of the formation of the austenite grains upon heating. He has shown how a nucleus forms within a pearlite island, and obviously the more numerous the pearlite islands, the more numerous the nuclei. We believe, however, that this mechanism applies principally to the very low carbon steels. In this connection I would like to present a few illustrations depicting the process of grain formation in S.A.E. 1045 steel, which is outside the strict scope of Dr. Grossmann's paper. I hasten to say, however, that in determining the two critical points by microscopic methods on a large number of steels, we have never seen an example which did not in principle follow Grossmann's scheme. His theory postulates the initial formation of moderately fine grains and the subsequent union of a number of these small grains to form larger grains. He follows

the grain growth very appropriately by expressing it in terms of the percentage of fine grains and of coarse grains. We believe that the vast majority of steels, and perhaps all of the low carbon steels, follow this pattern, though all steels may not do so.

We were particularly interested in Dr. Grossmann's finding that grain growth during carburization can proceed at a lower temperature or at a greater rate in the case than in the core. This seems to be one aspect of a general law; that if the pack carburizing can in any way reduce the resistance to grain growth, then the case must acquire a larger grain size than the core. On the other hand, if case carburizing, which is really carburization by carbon monoxide, can increase the resistance to grain growth, then the case must acquire a finer grain size than the core. Many steels have essentially the same grain size in both case and core.

A certain sample of S.A.E. 1045, plain carbon steel, which originally had a grain size of about No. 5, was normalized at the lowest possible temperature, 1470 degrees Fahr. (800 degrees Cent.), thereby acquiring a grain size of No. 7 as shown in Fig. 1 of this discussion. Normalizing this steel at 1740 degrees Fahr. (950 degrees Cent.) produced the microstructure shown in Fig. 2. In this case about 25 per cent of the material consisted of a No. 1 grain size, and 75 per cent of No. 6 and No. 7. This is in line with the customary mechanism shown by Dr. Grossmann. Normalizing at the unusually high temperature of 1920 degrees Fahr. (1050 degrees Cent.) produced an abnormally coarse structure, as shown in Fig. 3, consisting largely of No. 1 grains with a few grains of No. 2 or No. 3.

We have never seen an example in which the correlation between austenitic grain size and depth of hardening did not hold; namely, that the coarser the austenitic grain size of a given composition, the deeper the hardening. In other words, coarse grains are equivalent in effect to a deep hardening element such as manganese. Three bars, in which we had established a variety of austenitic grain sizes (existing at room temperature, of course, as pearlite grains nicely marked out with a ferrite network) were studied under identical hardening conditions, i.e., as quenched from a common temperature of 1490 degrees Fahr. (810 degrees Cent.). Fig. 4 shows how the conditions set up in the three normalizing treatments are reflected in the hardening behavior. We artificially created three grain size conditions, and it is evident that the coarsened steel hardened considerably more deeply. This chart is simply a succession of Rockwell readings across a number of diameters on 1-inch rounds, all of the Rockwell readings on the same concentric circle being averaged. The shallow hardening steel is the one which, as normalized, had the smallest grain size; the middle curve represents the steel with the mixed grain size, as normalized; and the deepest hardening steel is the one which had the coarsest grain size as normalized. The grain sizes established in the quenching operation are shown on the chart.

Carburizing these three bars gives us a slightly different grain size condition. The coarsened steel, normalized at 1920 degrees Fahr. (1050 degrees Cent.) produces the most normal appearance in pack carburizing, but the grain size of the core does not follow the rule that we have heard this morning. We

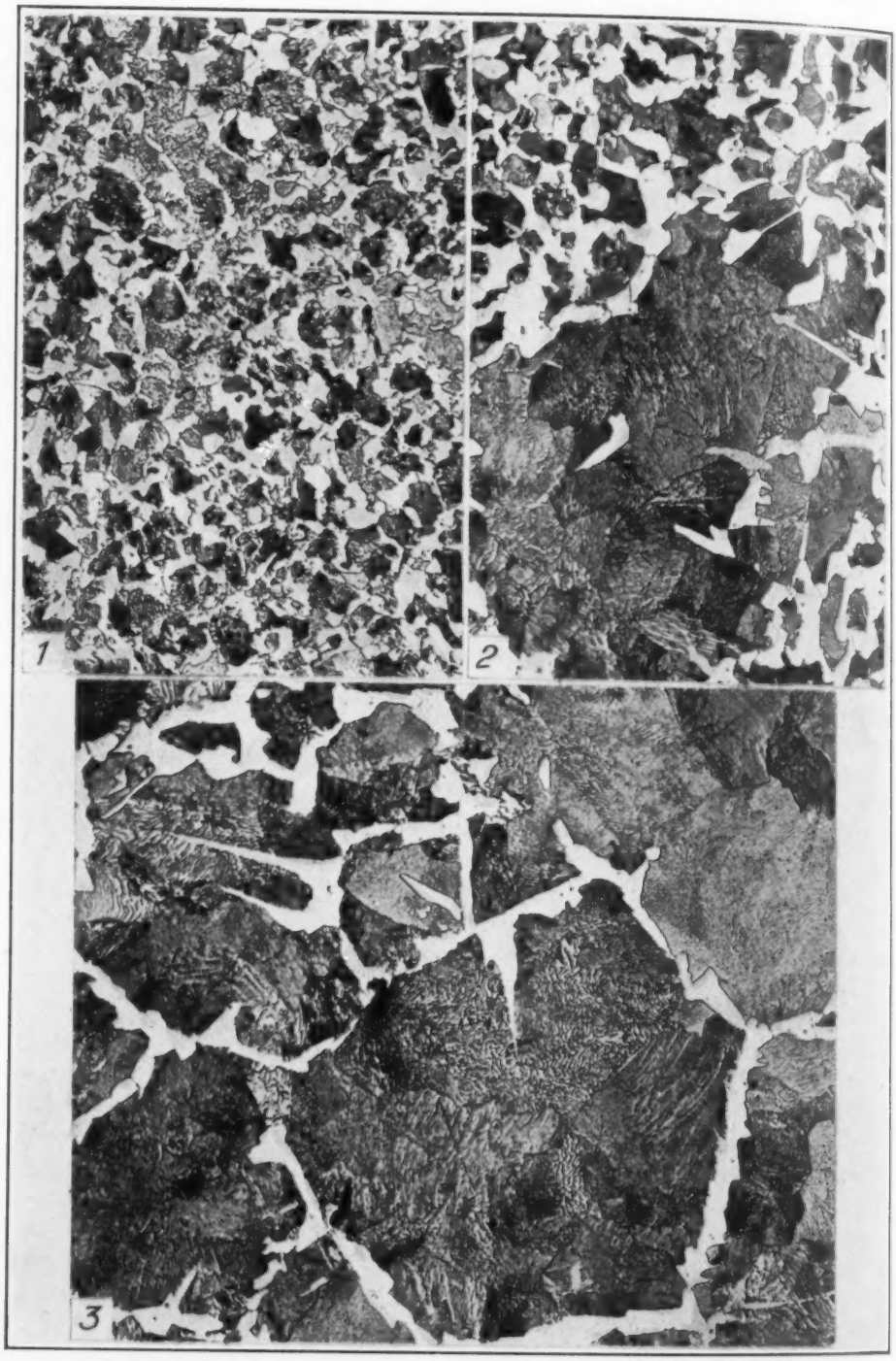


Fig. 1—S.A.E. 1045 Steel Normalized at 1470 Degrees Fahr. (800 Degrees Cent.) Grain Size 7. × 300.

Fig. 2—S.A.E. 1045 Steel Normalized at 1740 Degrees Fahr. (950 Degrees Cent.) Grain Size, 25 Per Cent 1 and 75 Per Cent 6.

Fig. 3—S.A.E. 1045 Steel Normalized at 1920 Degrees Fahr. (1050 Degrees Cent.) Grain Size 1 to 3.

believe this to be a case in which a large area of pearlite in the steel is somehow capable of forming not one nucleus, but several nuclei for the formation of the austenite grains on heating. The rule, therefore, appears not to hold always with very large areas of pearlite in which the austenite nuclei may form, and presumably it does not hold with higher carbon contents. The carburizing

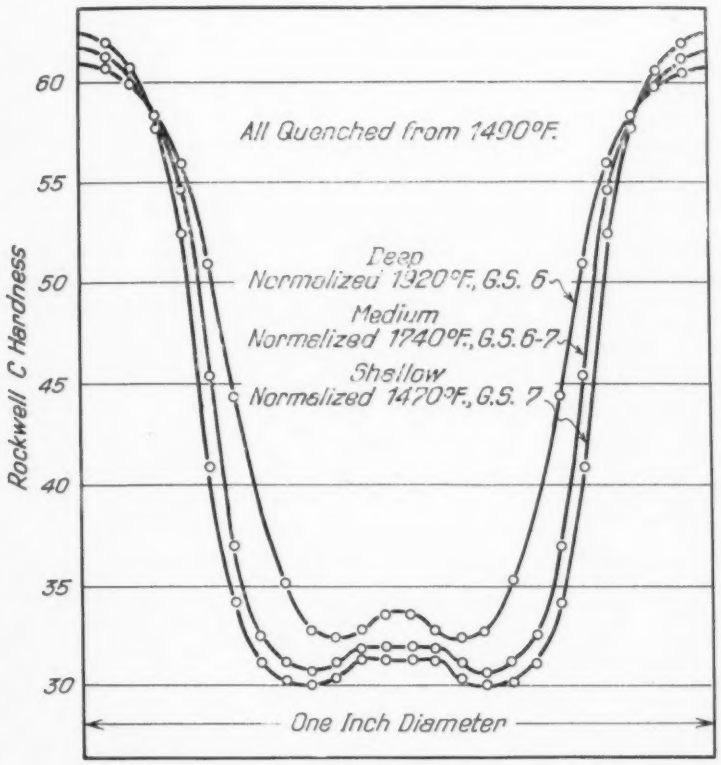


Fig. 4—Hardenability of S.A.E. 1045 Steel as Brine-Quenched from 1490 Degrees Fahr. (810 Degrees Cent.) after Previous Normalizing Treatments as Indicated.

treatment produced a mixture of 85 per cent No. 1 and 15 per cent No. 5 grains in the core of the steel which originally had the finest grain size (No. 7) as normalized. The steel of mixed grain size, as normalized, in carburizing acquired a core composed of 70 per cent No. 1 and 30 per cent No. 5, whereas the coarsest steel, as normalized, after carburizing had a core of uniform No. 5 grains.

While we believe that the majority of steels, and particularly the low carbon carburizing steels, exhibit the pattern of behavior described by Dr. Grossmann in which heating develops either fine grains or a mixture of fine and coarse grains, it is also quite possible with some steels to obtain with increasing temperature a series of grain sizes which varies from fine to coarse rather uniformly throughout each piece in the series. The hardenability of such a series is shown in Fig. 5 which depicts the depth of hardening in a 0.74 per cent carbon steel as quenched from the indicated temperature. Heated at 1375 degrees

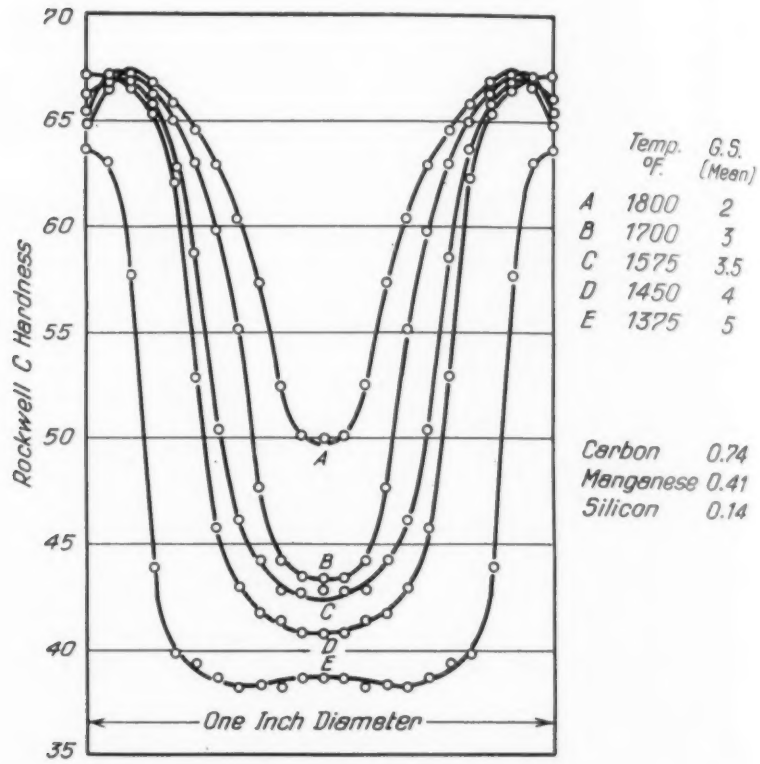


Fig. 5—Hardenabiiity of 0.74 Per Cent Carbon Steel as Influenced by Austenite Grain Size Brine-Quenched from the Indicated Series of Temperatures.

Fahr. (745 degrees Cent.) the material developed uniform No. 5; heated at 1450 degrees Fahr. (785 degrees Cent.) it developed fairly uniform No. 4; heated at 1575 degrees Fahr. (855 degrees Cent.) it produced a mixture of No. 3 and No. 5; at 1700 degrees Fahr. (925 degrees Cent.) it was nearly all No. 3; at 1800 degrees Fahr. (980 degrees Cent.) it consisted of nearly all No. 2. This is an example of a steel which, with higher and higher temperature, really takes on a definite uniform grain size at each temperature. As is clearly evident from the curves, the fine grains result in shallow hardening, while the coarse grains produce deep hardening.

Author's Closure

The author appreciates greatly the discussion by Mr. Epstein and that by Mr. Bain, and would like to say a few words in reply.

In Mr. Epstein's discussion, his point about grain growth during rolling seems particularly worthy of emphasis. The thought should indeed be extended to forging operations as well, for it is becoming more and more evident that actual grain size is the important factor, and that it may be affected by many of the operations to which steel is subjected.

As to our not discussing the effect of fine particles, we must point out

that this paper has nothing to do with inherent grain sizes, but only with the mechanisms of grain growth and variation (within the same steel). Also, we were well conversant with R. S. Archer's excellent paper of some years ago on the use of picric acid, and it is no detraction of that paper to remark that his method did not work on these steels.

Before proceeding to Mr. Bain's stimulating discussion, we must acknowledge a probable error, pointed out in a private communication by Mr. Bain and Mr. Davenport. We described the dark constituent in Fig. 6 as "pearlite just in the process of transforming," whereas they point out that it was probably a low-concentration austenite which has transformed to pearlite in cooling.

In Mr. Bain's Fig. 4, it is interesting that these pearlitic steels showed a grain size inheritance analogous to that in the steels which consisted largely of ferrite. The mechanism of transformations must be slightly different, because of the presence here of cementite, and yet the ultimate relationship is similar.

The interesting reversal of grain size, in which Mr. Bain showed the coarsest steels to give the finest structures after carburizing, constitutes an additional problem. We believe this to be due to still another mechanism, which has its counterpart in low-carbon steels, and on which it will be interesting to seek further elucidation.

ON THE DESIGN AND CONSTRUCTION OF A PRECISION HIGH POWER METALLOGRAPHIC APPARATUS

By Francis F. Lucas

Abstract

A new metallographic apparatus of advanced design is described. It was planned to make this microscope as perfect mechanically as possible and to incorporate in its design the most efficient optical systems that could be devised. Its resolving power is of the highest order with visible light. Crisp, brilliant images are secured at magnifications of 4000 to 6000 diameters. The specimen may be illuminated with monochromatic light, a narrow band or a broad filtered band of light from any region of the visible spectrum.

TEN years ago it was my privilege to present before this society a paper on high power photomicrography of metallurgical specimens. The following year, 1924, at the annual meeting of the society held in Boston, another paper was presented on the microstructure of austenite and martensite. In these two papers there was described the extension of the useful range of the microscope from a few hundred diameters to a few thousand diameters. It is perhaps appropriate after a decade's work in this particular branch of science to record again in the Transactions of this society some further developments and improvements in apparatus which will enable the metallographer to reveal the minute details of metal structures with greater exactitude.

One might assume that to extend the range of the microscope, radical and revolutionary changes in optics and principles would be required. This is probably more nearly true today than it was ten years ago. The development of high power metallography depended upon the fact that the available optics were not being used efficiently. Since the development of the apochromatic objectives of Abbe which occurred in 1886, science has had available an optical system capable of resolving about 140,000 lines per inch. That is

A paper presented before the Fifteenth Annual Convention of the society, Detroit, October 2 to 6, 1933. The author, Francis F. Lucas, is associated with the Bell Telephone Laboratories, Inc., New York City. Manuscript received July 27, 1933.

to say, if a ruling having 140,000 uniformly engraved and spaced lines were photographed under favorable conditions with these optical parts of N.A. 1.40, the lines should be resolved as individuals and each line clearly separated from its neighbors. There are but two well-recognized ways of improving resolution. To resolve a greater number of lines with equal brilliancy and sharpness of definition either the numerical aperture of the objective must be increased or the wavelength of the light used to photograph the specimen must be decreased. This very brief résumé will suffice for the purpose here. Those who are interested will find more complete discussions elsewhere.

All of these factors were well known and recognized years ago. Likewise it was known that the optical and associated parts of a photomicrographic apparatus must be solidly assembled to be free from vibratory disturbances or at least it must vibrate as a unit; the component parts of the apparatus must not vibrate independently. Exact optical alignment of the parts was also recognized as necessary.

It is a relatively simple matter to design a photomicrographic apparatus which will yield good results at low magnification. As the magnification is increased the difficulties mount. Longer exposures are required for higher magnifications unless more sensitive plates can be procured.

In 1927, the design of an advanced metallographic microscope became of interest. The plan was to make this microscope as nearly perfect mechanically as possible and to incorporate in the design the most efficient optical systems that could be devised. The plans were taken to Germany and discussed with the scientific staff of Carl Zeiss, Jena, where aid was sought in the final design and construction. The commission was accepted and work was started late in 1927. The actual design and construction of the apparatus required approximately four years, during which time close consultation with the makers was maintained.

The apparatus is an experimental one because the final answer could not be foretold on certain features of the design. Actually working with the apparatus constituted the final test. The equipment was delivered in New York in May, 1931, and by late summer was installed in a laboratory especially prepared to receive it. Some details of the installation and of the laboratory will be de-

scribed, since they may be of interest in connection with the arrangement of photomicrographic laboratories in general.

About the time this apparatus was being designed, the Zeiss Company announced a new system of apochromatic objectives corrected for infinity tube-length rather than for a fixed tube-length of 190 millimeters, as had been customary practice with that company. These objectives, it was believed, would yield better images for reasons which will be given later. Experimental evidence was desired, since all of our work had been accomplished with the objectives corrected for 190-millimeter tube-length. If the older type objectives were abandoned and the apparatus designed only for the new infinity objectives, there would be no basis for comparison. For this reason, the microscope was designed to take either type. Experience with the apparatus seems to have demonstrated conclusively that the infinity corrected objectives are superior in the photographic results which they yield and these objectives are now being used exclusively. For this reason a description of the arrangement of the apparatus for the objectives corrected for 190-millimeter tube-length will not be included.

In other publications[1, 2] it has been shown that the color of the light which is used to photograph a given metallurgical specimen may have a very important bearing on the detail revealed in the photograph, due to the selective absorption of the light by the different constituents in the metal specimens. Experimental evidence has substantiated the conclusion reached years ago that a decrease in the wavelength of light used is a potential factor in increasing resolution. It has been demonstrated that a given detail photographed with blue light will appear somewhat sharper than with red or green light. If selective absorption enters into the problem it will be manifested when the color of the light is changed.

Selective absorption plays a part because contrast is accentuated or diminished. If a constituent absorbs blue light and the background reflects it, the short wavelength not only increases resolution but also promotes contrast. However, if the constituent absorbs red light and both the background and the constituent reflect blue light, better photographic results may actually be achieved by using red light in preference to blue.

[1] F. F. Lucas, "On the Art of Metallography," *Mining and Metallurgy*, May, 1931.

[2] F. F. Lucas, "Advances in Microscopy," *Proceedings*, Zurich Congress, International Association Testing Materials, September, 1931.

The designation, "lines-per-inch," as a measure for resolution is not a very fortunate one because few specimens exhibit a uniform arrangement and spacing of detail. Perhaps the nearest approach is in the age hardening (or softening) phenomenon of metals in which a hard constituent is precipitated from the matrix in a very fine particle size—so fine that we see millions of particles only as a cloud. These particles under suitable treatment may be induced to coalesce and to grow in size so that they may easily be recognized at low powers as single particles. The utmost in resolving power is required to reveal the very fine particles.

When a filter is spoken of as transmitting a certain dominant wavelength, it is meant that the light which it transmits is maximum at the dominant wavelength. The filters ordinarily used in metallography transmit "zones" in the spectrum. For example, a filter may transmit blue light from 4000 to 5000 Å.U., but its dominant wavelength may be 4500 Å.U. So in photographing with filters, one does not use single wavelengths of light or a limited group of wavelengths, but a broad band of wavelengths the intensities of which may gradually increase from zero to a maximum and then decrease again to zero. Keeping in mind that the very best apochromatic objectives are only an approximation at bringing all of the different wavelengths to a common focus, it becomes apparent that in a precision metallographic apparatus means should be available for accurately controlling the wavelength of the light. If it is desired to work with light of a given wavelength, it should be possible to exclude all other wavelengths. In theory, at least, the objective should be able to function better if all wavelengths other than the particular ones desired are excluded. A further advance in this direction would be to have, instead of apochromats, "monochromats," i.e., an objective with very fine spherical correction for a given wavelength of the spectrum. When used with the particular wavelength for which it was corrected the definition should be of the highest order, because many approximations in the correction of apochromats for the entire visible spectrum are thereby eliminated. Chromatic errors do not occur, because the objective is confined to a single wavelength for which a high order of spherical correction can be attained.

In this particular apparatus, a step has been taken in this direction by making use of the monobromnaphthalene objective of N.A.

1.60 which Professor Kohler has now corrected for the blue region of the visible spectrum. This metallographic objective probably represents the highest achievement yet attained in the correction of a high aperture objective for a restricted region of the spectrum. Some years ago the author revived interest in the monobromnaphthalene objective which for years had been practically abandoned. Professor Kohler[3] produced several for the yellow-green region of the spectrum and, as previously stated, has now corrected objectives for the blue region. This permits one to employ the shorter wavelengths with these very high aperture objectives. These objectives, so far as practical application is concerned, are still in the experimental stage. Results thus far are promising.

If the intensity of the light is decreased by using monochromatic light or a very narrow group of lines, a much longer exposure will be required to secure a photographic negative of proper density, assuming the same plates are employed as when using a broad band of filtered light from the spectrum of an arc lamp. Heretofore the exposure was limited to about one and one-half minutes because the equipment lacked the mechanical stability which would permit longer exposures. In this new metallographic equipment, much thought was given to mechanical stability in order that longer exposures could be made.

The Eastman Kodak Co. has recently developed a "metallographic plate" which is more sensitive to the blue and the green regions of the spectrum than other types of plates. These metallographic plates have simplified the problem and they are ideal in quality. For the red end of the spectrum, the Wratten M plate or the red sensitive spectroscopic plates are used.

Thus if we summarize the desirable characteristics in a precision metallographic equipment for photographing at magnifications from 4000 to 6000 diameters, we require great mechanical stability, freedom from creep, absolute freedom from outside disturbances, the means to illuminate the specimen with light of any selected wavelength or group of wavelengths within the visible spectrum, and the highest order of achievement in optical equipment. Notwithstanding the time, care and thought given to the development of this equipment, the desired result has not been fully achieved in all cases.

The entire equipment is mounted on three stands as illustrated

[3]Professor A. Kohler, "General Microscopic Objects," *Methodik der wissenschaftlichen Biologie*, Vol. 1, 1928.

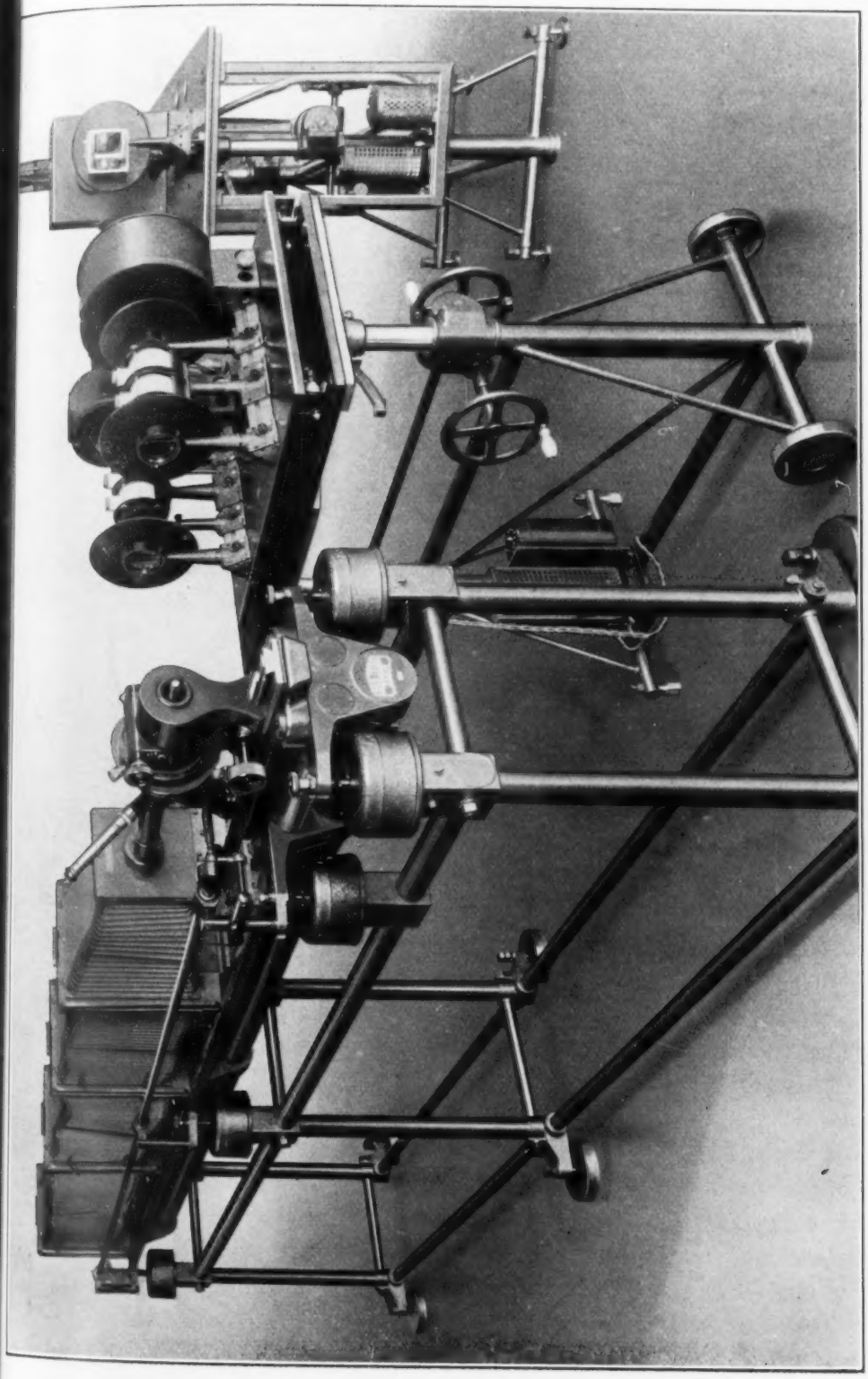


Fig. 1—Zeiss Precision High Power Metallographic Apparatus after Lucas, Designed and Developed by Bell Telephone Laboratories, Inc., in Co-operation with the Firm of Carl Zeiss, Jena, Germany.

in Fig. 1. Great difficulty would be encountered in eliminating vibration and in freeing the equipment from outside mechanical disturbance if the apparatus were mounted on a single stand. As assembled it measures about twelve feet in length and about ten feet in breadth.

The microscope and the camera are mounted on one stand which has six supports provided with levelling screws and resting on six cast iron disks which in turn are insulated from the floor by sponge rubber pads. The camera and the microscope are assembled on a carrier consisting of three large tubes which at their ends and at two intermediate points are rigidly joined together by massive yokes. Each yoke or tie piece has two laterally extending arms. These arms are fitted with large screws with knurled heads and each screw rests on a shock absorber, making a total of eight shock absorbers. When the screws are turned down the shock absorbers do not function, but when they are turned up the carrier rests on the shock absorbers. The two upper tubes of the carrier serve as rails for the camera.

The camera is in four sections in order that any length bellows extension may be secured. At the right of the camera is a metal scale graduated in centimeters and running the entire length of the camera bed. On each camera section is mounted a small millimeter scale which acts as a vernier. The centimeter scale and a vernier scale give the correct length of the bellows extension. Each camera section is provided with a clamping device. This clamping device grips the rails or releases by turning a substantial lever on or off as the case may be. Each of the three rear camera sections is provided with short straps so that the sections not in use may be pushed together and the bellows held compressed by snapping an eyelet in the end of each strap over a button fastened to the forward frame of the camera section. If two sections of the bellows are in use, the other two may thus be compressed and slid back out of the way on the rails. The maximum plate size of the camera is 24 by 30 centimeters and this may be reduced by suitable kits to accommodate 8 by 10 inch, 5 by 7 inch, 4 by 5 inch or 3¼ by 4¼ inch plates. The camera is mounted so that the holders and screens slip in from above. This arrangement is more convenient for focusing when short bellows extensions are used and by inserting the plates and holders in a vertical direction, there is less likelihood of inducing vibration. The camera mounting is compact and the arrangement has given entire satisfaction.

The microscope is arranged horizontally because, in the author's opinion, the design simplifies construction of focusing mechanism, reduces the number of prisms and optical surfaces to a minimum, is more substantial and the component parts are less subject to creep. The horizontal arrangement is not as convenient to work with as a

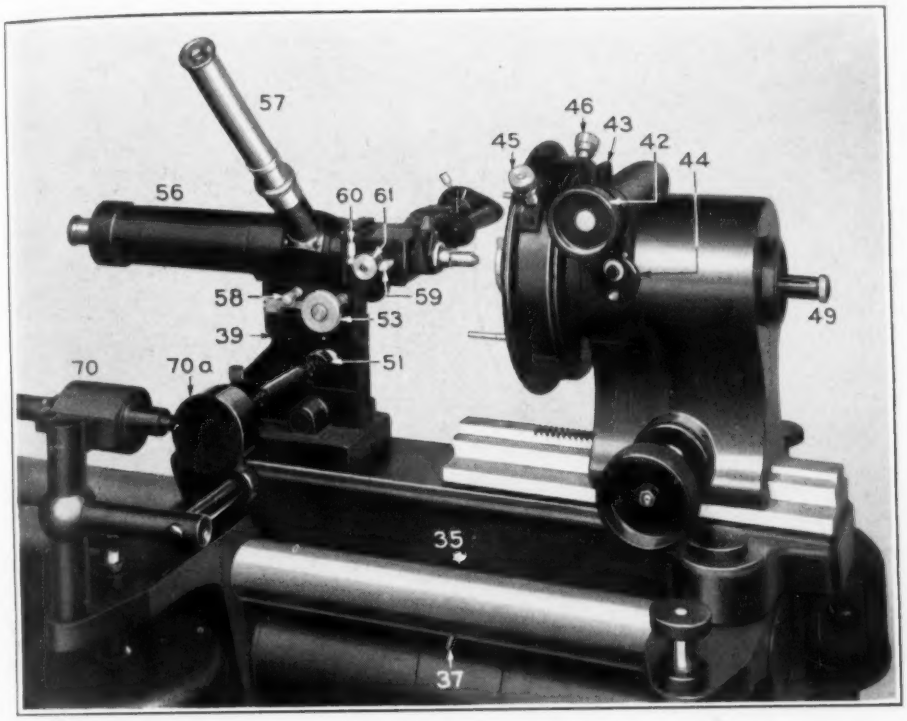


Fig. 2—Microscope Assembly from the Observation Tube Side.

vertical or an inverted type microscope. In this precision instrument maximum stability and the minimum number of delicate moving parts are desired. In a routine instrument, convenience would be more of a factor.

The microscope has a heavy metal base, 35, which may be more clearly seen in Figs. 2 and 3. The base is of triangular cross section and rests tension-free upon three points. Three hardened steel balls are mounted in holders—two rest on the first connecting yoke and one on the second yoke. The microscope, which is massive and properly balanced with reference to its center of gravity by the triangular base, rests on the steel balls. The ball mounting is such that the microscope assembly comes to rest in one position. A small pin, 37, passing through the base and projecting so as to strike the mounting

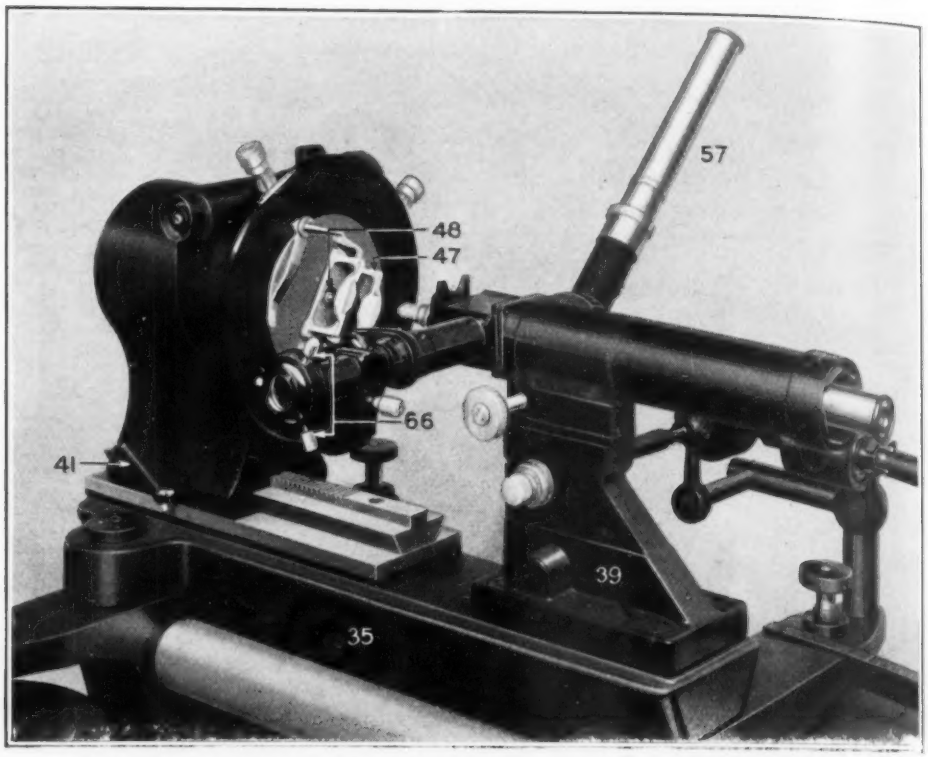


Fig. 3—Microscope Assembly from the Vertical Illuminator Side.

rails (two upper tubes) if the microscope is lifted or forcibly displaced, acts as a safety device. By removing the safety pin the whole microscope can be lifted from its mounting.

The stage is massive and is mounted as a separate assembly on a stage carrier plate which is screwed to the triangular base plate. A very sturdy rack and pinion mechanism for coarse focusing of the stage is provided and may be locked in any desired position by a lever mechanism, 41, shown in Fig. 3. The stage revolves about a long horizontal axis within the upper part of the stage carrier. If desired it may be rapidly turned by hand or slowly by means of a knob, 42, which is shown at the top of the stage assembly in Fig. 2. If it is desired to revolve the stage by hand a latch, 43, releases the gears and they are held released by operating a catch, 44.

Two thumbscrews shown at the top of the stage, 45 and 46, allow the object to be displaced in two directions at right angles to each other similar to the movement of certain types of mechanical stages. The movement is not fixed as horizontal and vertical. As a result the specimen moves diagonally. Experience with the apparatus

has shown conclusively that this is a distinct disadvantage, and oftentimes a serious annoyance.

The mechanical stage movement is along modern conventional lines of microscope construction; experience has demonstrated that an instrument of this kind requires precision machine tool construction. Soft metals and delicate conventional microscope movements are not suitable. What is required is a movable stage actuated by two precision screws, one operating vertically and the other horizontally. Both screws should be substantial as to size and should be of steel. The stage plate should slide on massive ways. By means of a suitable gearing mechanism the stage plate should be capable of being revolved on a substantial collar about its axis and of being securely locked in any position.

The object is held in special interchangeable holders, 47, with surface exactly parallel to the stage. A holder is selected to suit the dimensions of the specimen. It is then fastened to the stage by two locking screws. The specimen is slipped in back of the parallel surfaces and is held against these surfaces by a single point contact, 48. The contact or stud is under spring tension and is drawn back by a rod terminating in a knurled knob, 49, at the rear of the stage. This is a method of mounting developed and fully tested in Bell Telephone Laboratories before this equipment was designed and is the only mounting which the author has found fully satisfactory for his work.[4] Its construction has been described elsewhere.

To the opposite end of the base plate is fastened the tube carrier, 39, which is provided with a standard slow motion, 51, of the cog-wheel type conforming to the design used on all recent Zeiss microscopes. The slide which is controlled by the slow motion supports the rack and pinion movement of the tube. This is the conventional coarse adjustment, 53, of the ordinary microscope. The rack and pinion movement carries at its forward end a vertical plate to which the vertical illuminator is fastened with screws. The microscope tube, 56, slides into suitable ways of the rack and pinion movement and butts against the vertical illuminator where it is held securely in position by a clamping mechanism, 58. As has been previously mentioned, this whole microscope assembly is of experimental construction and the reason for mounting the tube as described was to make it

[4] F. F. Lucas, "A Resume of the Development and Application of High Power Metallography and the Ultra Violet Microscope," *Proceedings*, International Congress Testing Material, Vol. 1, 1928.

interchangeable with a 190-millimeter tube. Since the infinity objectives have been demonstrated to be superior to the 190-millimeter tube-length objectives, the need for this interchangeability of tubes no longer exists.

The vertical illuminator is now capable of simplification as it was designed to accommodate both types of objectives. It is fitted with a plane parallel glass plate, inclined at an angle of 67½ degrees rather than the usual 45 degrees. This is the optimum angle for maximum reflection and has an appreciable effect in increasing the illuminating efficiency of the system. This plate is adjustable within certain limits. Screw 59 changes the tilt of the plate toward the axis of the microscope. Screw 60 turns the carrier with the plate around the axis of the microscope and screw 61 displaces it within the deflection plane at right angles to the axis of the microscope.

Mounting the glass plate at an angle of 67½ degrees would require a change from a right angle assembly of the illuminating units. To overcome this, a small prism is incorporated in the illuminator to correct the deflection of the rays so that a right angle assembly of the illuminating units may be employed. The tube of the illuminator contains the lenses and diaphragms regulating the path of rays. At the outer end of the vertical illuminator tube is a short sliding sleeve provided with centering screws, 66. Into this fit two short sliding tubes in each of which is mounted a condensing lens of suitable focal length. One is provided for use when the first illuminating system is employed (the arc lamp or mercury vapor lamp) and the other for the monochromator.

The microscope tube is provided with an observation tube (57) which is fitted at its base with a simple reflecting prism. When the observation tube is pressed downward the prism intercepts and deflects the rays on to an eyepiece for observation. When the observation tube is withdrawn the rays continue through the main tube, producing the image on the focusing screen or the photographic plate. The observation tube is provided with centering adjustments. Sliding objective changers of the conventional Zeiss design are provided for the objectives.

A remote focusing device, 70, extends along the right side of the camera. It consists of three rods connected by universal joints and running in ball bearings. A turn of the rod moves a small gear set mounted in a closed gear case, 70-a. A reduction of 1:4 is thus

accomplished. While the microscope tube and vertical illuminator assembly differs outwardly from those of other conventional equipments, it is nevertheless built up of standard microscope parts and, like the stage assembly, the tube assembly has proved unreliable. Soft metals and delicate moving parts, conventional rack and pinion movements, conventional slow motions and tube mountings of diaphragms and condensers of the illuminating system do not maintain adjustments for precision work. Experience has demonstrated that it would be desirable to redesign the microscope along machine tool lines.

Experience suggests a design which would consist of an optical bench with saddle stands to carry the objective changer, the prism and plane glass reflector assembly, the observation tube and the projection ocular. The vertical illuminator parts should be assembled similarly on a suitable optical bench and every part should be capable of being optically centered and aligned, and once so adjusted, they should be capable of being rigidly locked in position. The whole assembly should then be provided with a removable metal cover having a suitable aperture to admit the illuminating beam. The slow motion should take the form of a precision screw with a suitable gear set for a reduction of 1:4 and the slow motion should control the optical bench. With proper selection of modern metals such an instrument can be made which should function properly and yield results of the highest order. The present microscope is workable, will maintain adjustments reasonably well and the equipment as a whole has yielded the best results achieved to date.

Two illuminating stands with elevating gear for vertical adjustments of the illuminating beams are provided. The stands are so arranged that they may be moved on rollers for horizontal adjustments. It will be observed that the illuminating stands are not safeguarded against outside disturbances as was done with the camera and microscope stand. This was avoided by designing the optical system in such a way that the beams would always cover the aperture diaphragm opening of the vertical illuminator. Vibrations or disturbances which arise or are induced in the illuminating stands have no effect whatsoever on the image as photographed.

The first illuminating stand, Fig. 4, has a table top which slides on rails. It carries two optical benches parallel to each other and so mounted that, when the table top is run on the rails until it strikes

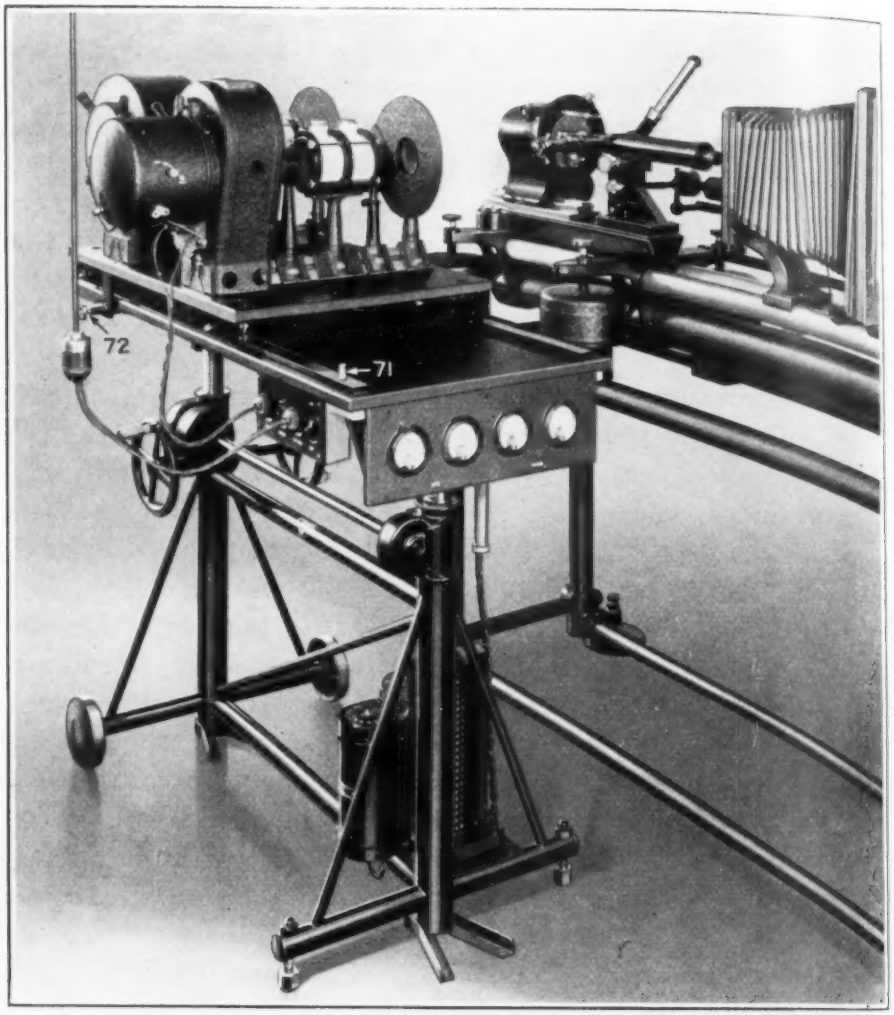


Fig. 4—First Illuminating Stand, on which are Mounted Two Optical Benches. One Illuminating System Operates from an Arc Lamp and the other from a Mercury Vapor Lamp.

a fixed stop in the direction of the microscope stage, the arc lamp train is brought into alignment (after once being properly adjusted) with the vertical illuminator. By releasing a catch, *72*, the table top may be moved in the opposite direction until it strikes another stop, *71*, in which position the optical train of the mercury vapor lamp comes into adjustment with the vertical illuminator. On the stand is mounted an instrument panel, switches and rheostats for controlling the voltage and current of the lamp circuits. The arc lamp is the standard clock feed type. It operates at a voltage of 55 and a current of 5 amperes. Small voltmeters and ammeters on the instrument

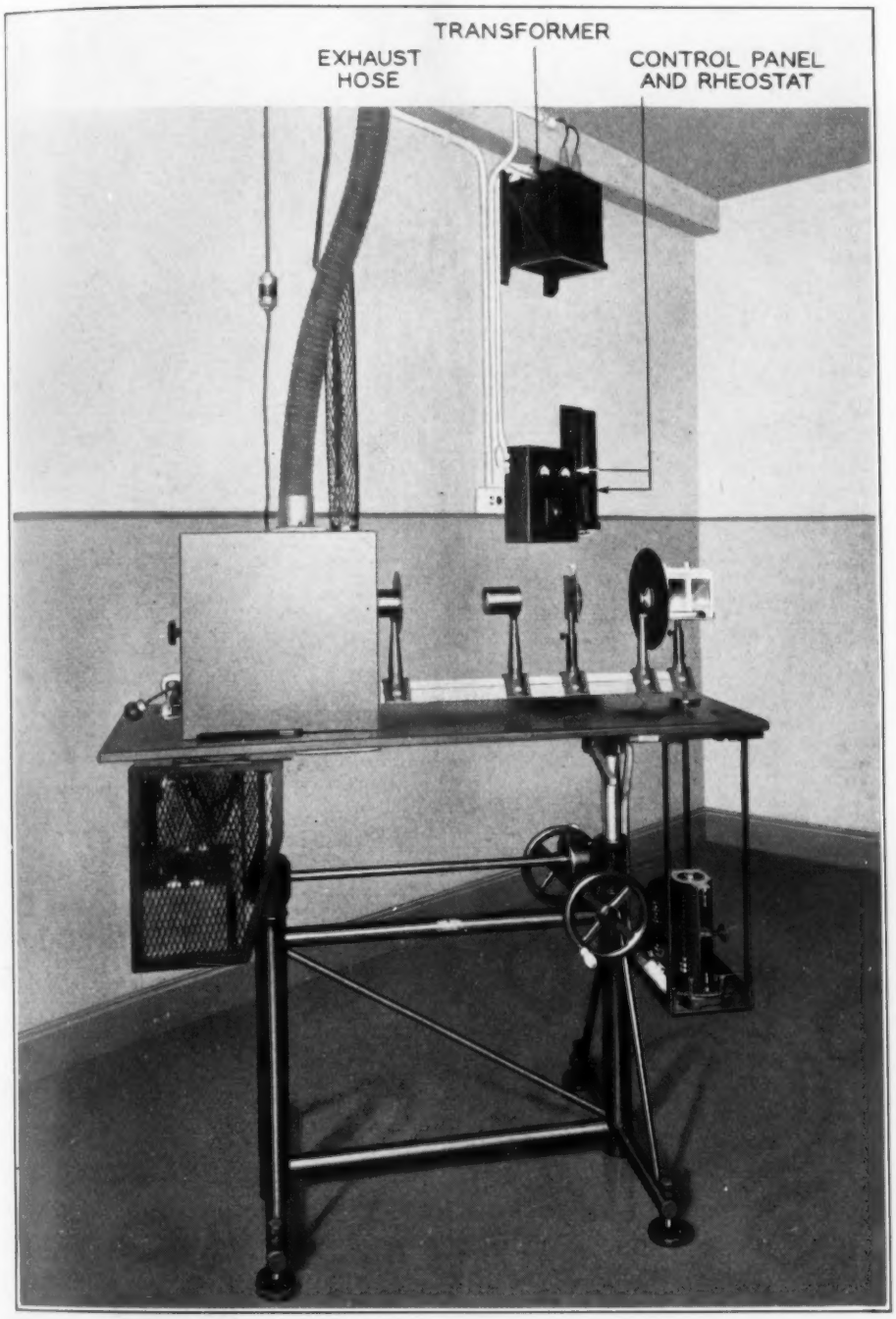


Fig. 5—The Second Illuminating Stand or Monochromator Arranged to Use the Spark Generating Apparatus.

panel show whether the correct electrical conditions are being maintained. The arc lamp train is the most intense source of illumination

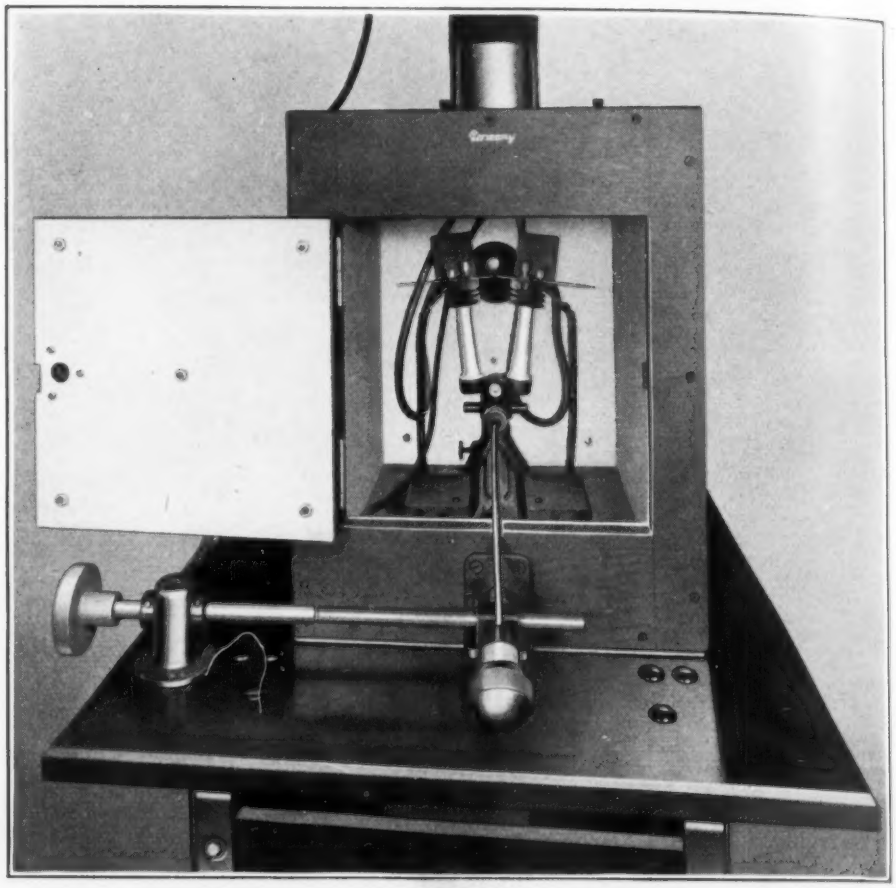


Fig. 6—Electrode Holders and Details of the Spark Gap.

and is used in conjunction with Wratten filters. The mercury vapor lamp train in conjunction with filters provides an approximately monochromatic means of illuminating the specimen with the strong mercury vapor lines.

When the movable table is placed in a midway position the path to the vertical illuminator is unobstructed and the monochromator may be used as a source of illumination. The monochromator is designed to operate with two sources of illumination, a spark gap or a mercury vapor lamp.

The assembly of the apparatus for the spark gap illuminating train is shown in Fig. 5 and details of the electrode holders in Fig. 6. Flat metal strips are used for the electrodes and, by using the appropriate metal, any strong line or group of lines may be isolated from the visible spectrum. The spark gap is covered by a wooden box lined with sheet metal and heavy felt for deadening the noise of the spark.

The box has a large flexible hose connecting with an exhaust fan and flue so that the atmosphere within the box may be kept clear and also to guard against dangerous fumes getting into the atmosphere in the laboratory and thereby producing a health hazard. The exhaust fan which is mounted near a distant flue to the roof of the

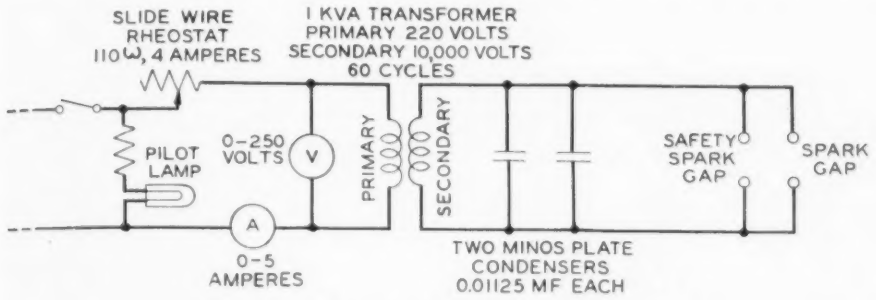


Fig. 7—Electrical Circuit of Spark Generator.

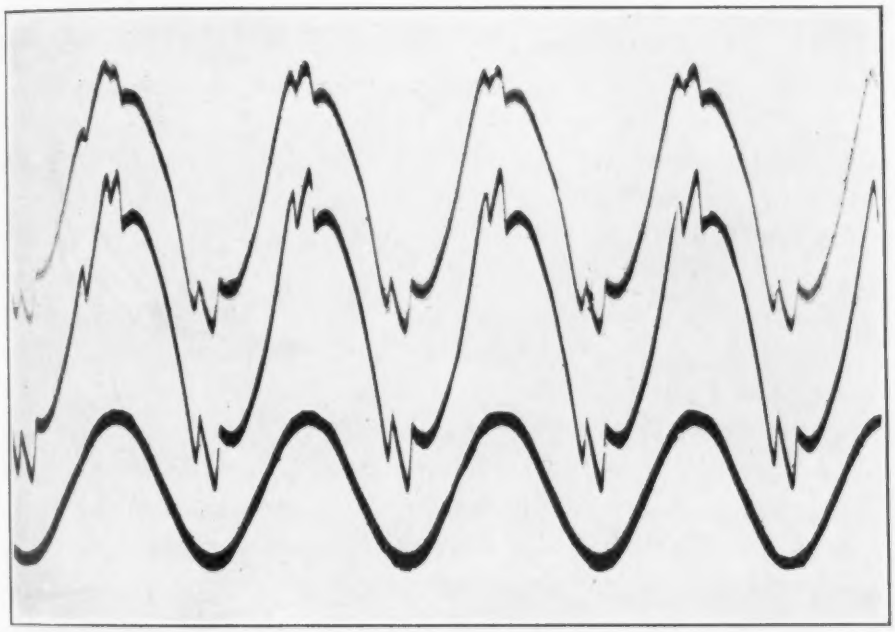


Fig. 8—Oscillograph Records of the Wave-form for Service Voltage (lower record); the Current in the Primary Circuit (middle record); and the Current in the Secondary Circuit. Oscillations at Crests Show Duration of Spark.

laboratory building is controlled by a switch mounted on the wall adjacent to the power panel. When the exhaust is in operation a green signal lamp mounted with the switch is illuminated. The lamp can be seen from all parts of the laboratory room. The optical train in addition to the spark gap apparatus consists of suitable condensers,

an adjustable slit and a large hollow prism. All are mounted on a movable optical bench which may be turned through an arc. The pivot providing the center of rotation is mounted directly beneath the prism. Rotation is by means of a threaded rod and collar operated by a large hand wheel as shown more clearly in Fig. 6. The hollow glass prism is filled with carbon disulphide, monochlorbenzol, or any other liquid of the required index of refraction. The light emitted by the spark is decomposed spectroscopically by the optical train into the characteristic line spectrum of the metal used as electrodes. By movement of the optical bench through its arc of travel any desired line may be brought to bear on the vertical illuminator and all others excluded. A type D Hilger spectrometer is used as a means of control for wavelength. The lines are about six inches in height. When a given line is focused on the vertical illuminator a portion passes over the illuminator and is picked up by the spectrometer which is mounted on a table provided with casters in order that the instrument may be easily aligned with the light source.

The electrical circuit of the spark generator is shown in Fig. 7. In Fig. 8 are reproduced oscillograph records of the wave-form for primary current and voltage, and the secondary current.* Experiments made in the laboratory seem to indicate that an increase in the frequency of the supply to the transformer has little practical effect on the intensity of the illumination.

We have concluded that the only practical way in which to secure greater intensity of illumination is to put more energy into the system. The present design of spark gap allows but a limited loading of the electrodes.[5] Professor Kohler has proposed a rotating type of electrode in which, he states, the discharge does not wander and, because of the rapid rotation of the electrodes, the heat is dissipated so rapidly that the current loading may be very high.

The condensers and safety spark gap are mounted on a frame suspended from the under side of the table top and are guarded by wire mesh. The electrode feed is by means of a flexible cable shown in Fig. 6. The optical bench and the metal frame of the stand are grounded by a cable.

The transformer supplying the power is mounted near the

*For the sake of clarity, the curve for secondary current is displaced 180 degrees as to phase.

[5]A. Kohler, "Some Innovations in the Field of Photomicrography with Ultra Violet Light," *Die Naturwissenschaften*, Vol. 21, 1933.

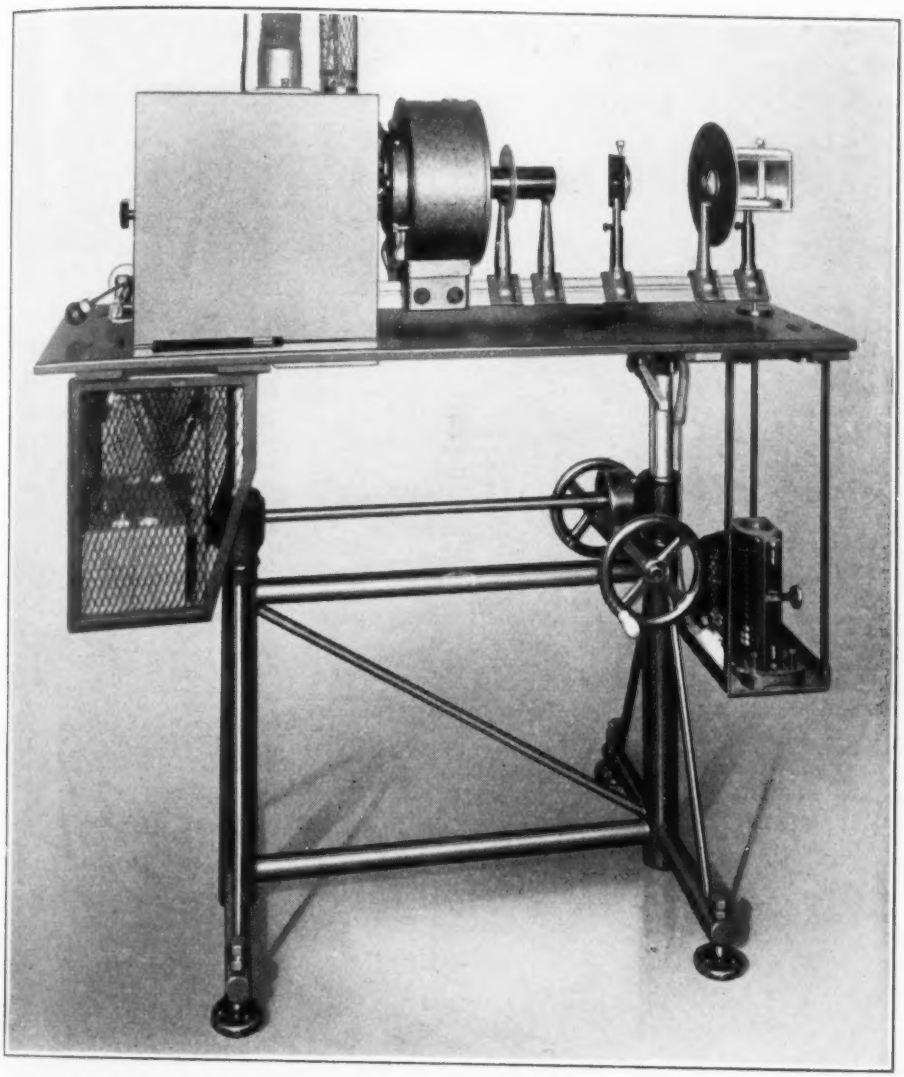


Fig. 9—The Second Illuminating Stand or Monochromator Arranged to Use the Mercury Vapor Lamp in Place of the Spark Generator Apparatus.

ceiling of the laboratory and the high tension leads are brought to the spark apparatus through conduits and metal guards. The power panel conveniently located on the wall of the laboratory has a switch controlling the primary supply to the transformer, a red pilot lamp which can be seen from all parts of the laboratory room when the power is on, and a voltmeter and ammeter showing voltage and current of the primary supply. A rheostat mounted to the right of the power panel controls the current in the primary circuit. Normal operation is at 2.25 amperes but the electrodes will stand loading to

about 3.5 amperes which is used when maximum intensity of illumination is desired.

In Fig. 9 is shown the arrangement of the monochromator when the mercury vapor lamp is used in place of the spark generating apparatus. The mercury vapor lamp is mounted directly in front of the

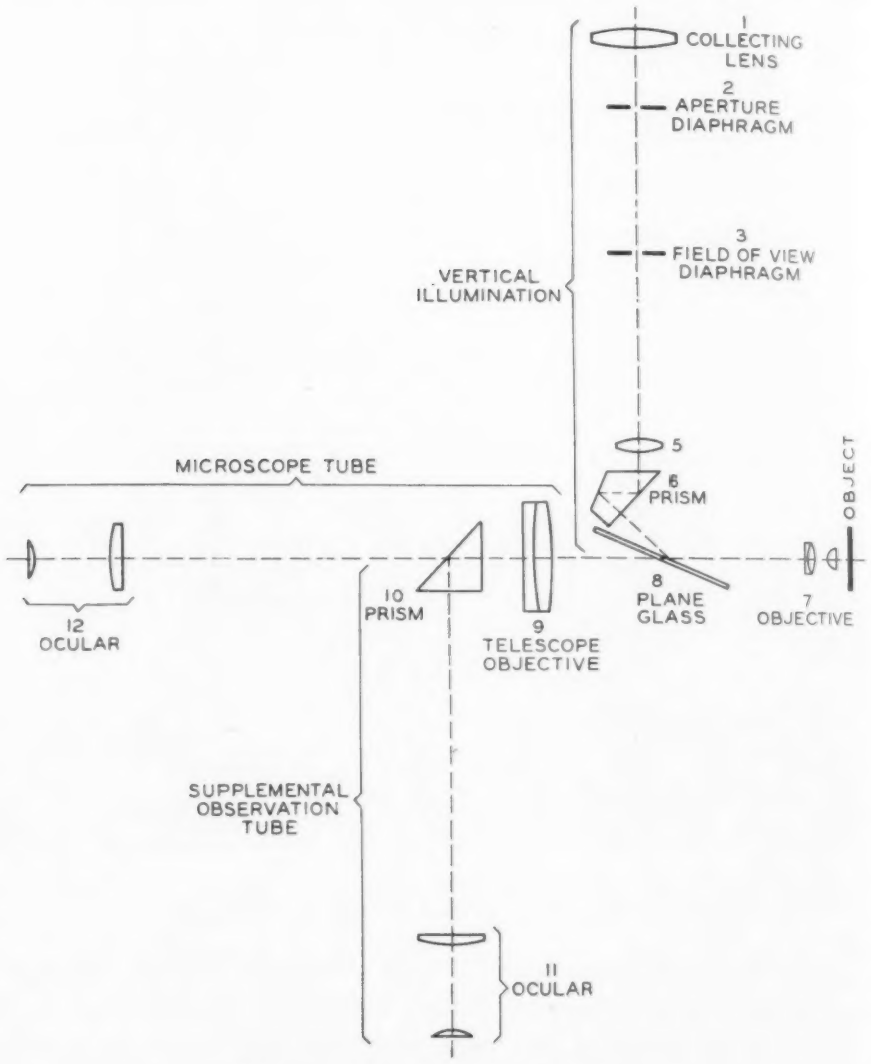


Fig. 10—Optical System of the Microscope.

spark fume hood. There is a slight change in the condensers but otherwise the optical system is identical with the one employed with the spark generating system. Electrical meters for voltage and current readings of the lamp circuit are mounted flush in the table top on the side opposite to the one shown in the illustration. Plug re-

ceptacles and switches controlling the lamp and service connections are also mounted on the table top near the meters.

In Fig. 10 is shown a much simplified diagram of the optical system of the microscope. From an object situated in its focus, objective 7 produces an image in infinity. This image is viewed through a Keppler telescope consisting of objective 9 and ocular 11 or 12. If prism 10 is lowered to the position shown, the image is directed to the lateral eyepiece 11 of the observation tube but if it is withdrawn the image is directed to eyepiece 12.

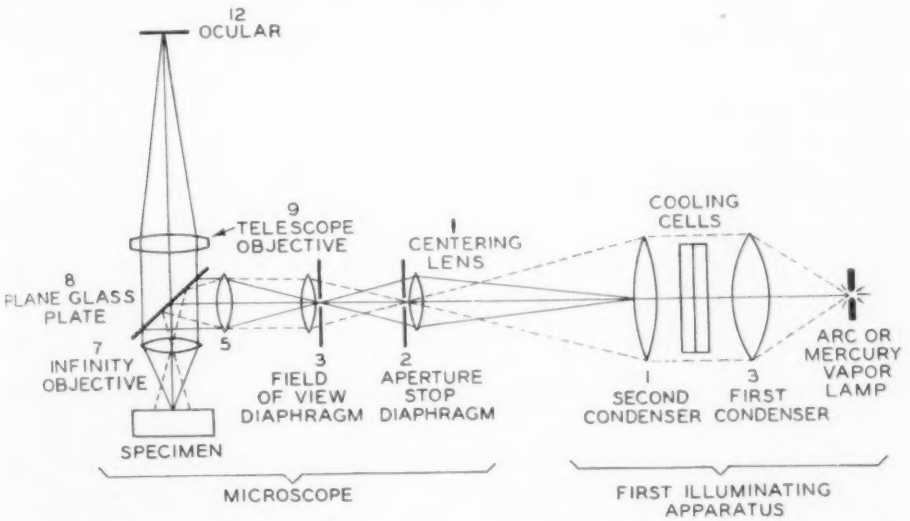


Fig. 11—Optical Diagram of the Paths of the Rays in the Microscope and the First Illuminating Stand when the Mercury Vapor Lamp is Used.

The magnification of the lens image produced by the objective alone and situated at infinity is equal to 250 millimeters divided by the focal length of the microscope objective. This image is magnified by the telescope, the magnification of which is equal to the focal length of the telescope objective divided by the focal length of the eyepiece.

According to Professor Kohler this arrangement, employing infinity-corrected objectives and a Keppler telescope in place of 190-millimeter objectives and an ocular, has the advantage that the vertical illuminator may be inserted at a place where the rays are parallel. When the rays are parallel the plane glass plate of the vertical illuminator reacts alike on all rays without interfering with their original correction. When using objectives corrected for 190-millimeter tube length, the cones of light passing through the plane glass have a finite, though small, aperture angle. The disturbing influence

of the plane glass then becomes more pronounced the higher its index of refraction and the narrower the angle at which it is set to the axis.

Between 9 and 7 the plane glass plate 8 of the vertical illuminator is placed. The reflecting power of the plane glass plate is increased when the reflecting angle of 45 degrees is exceeded. A reflecting angle of 67½ degrees was used because it brings the reflecting power to about 50 per cent of the incident light which is the most favorable value. The efficiency of the illuminating system is thereby increased.

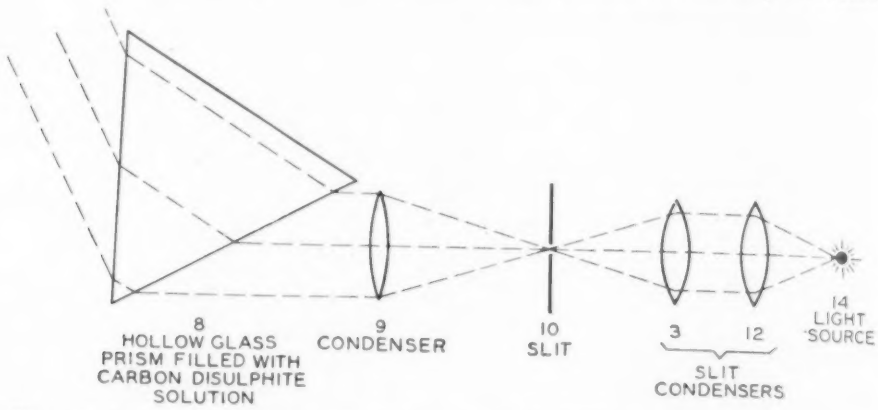


Fig. 12—Path of Rays in the Monochromator when Mercury Vapor Lamp is Used.

In order to facilitate the arrangement of the illuminating apparatus and to employ incident light at right angles to the microscope axis, prism 6 is placed in position to correct the angular arrangement.

Lens 5 projects an image of the radiant (field of view) diaphragm 3 in infinity. This image of the radiant field diaphragm situated in infinity, after being reflected by the prism 6 and plane glass 8, is again imaged in the object by the objective. The same lens 5 projects an image of the aperture diaphragm, 2, in the upper lens of the microscope objective 7.

Fig. 11 is a simplified optical diagram showing the paths of the rays in the microscope and the first illuminating stand when the mercury vapor lamp is in use. In this diagram the dimensions and spacing of the component parts are not in their true relationship. The plane glass plate is also shown at an angle of 45 degrees and the prism which corrects the deviation of the rays is also omitted for the sake of clearness. It will be observed that the rays, where they pass through the plane glass, are parallel and that the telesc ɔe objective brings them to a focus within the ocular. When objectives

corrected for 190-millimeter tube length are used the rays, as they pass through the plane glass, comprise a converging cone.

The path of rays in the monochromator is shown in Fig. 12. It is assumed that the source of light is the mercury vapor lamp. The first member of the slit condenser produces an image of the source of light at infinity. This infinitely distant image is reproduced on the slit 10 by the second member of the slit condenser 3. The image of the slit 10 together with the second image of the source of light is formed on the aperture stops of the vertical illuminator of the microscope. Immediately after passing condenser 9, the rays pass through the hollow glass prism, and the image of the slit is dispersed into the various monochromatic slit images of which it is composed.

This equipment was designed as a high power metallographic apparatus; and objectives of the very highest resolving ability are employed. However, it is generally desirable to observe and oftentimes to photograph structures at low powers. For this reason we have included with the apparatus optical parts which will allow a range in magnification from 100 to 6000 diameters. A very high grade, low power projection ocular is used as the eyepiece of the Keppler telescope.

A special laboratory was prepared to receive the apparatus. Since the equipment is used in a darkened room, it is desirable to see the outlines of the apparatus. If people are present as observers or spectators, and are not familiar with the apparatus, they may do serious damage by moving about in the dark. The apparatus itself is finished in black, for no other good reason than that black is a standard finish and precedent seems to have decreed it. However, it would have been far more logical to have finished the apparatus in white or a light color so that the framework and other parts could be seen in a darkened room.

The ceiling and upper two-thirds of the walls of the laboratory have been enameled a cream color; the lower third of the walls, a yellow-green. Physiologically the yellow-green rays are the most effective. Thus by painting the walls in cream and yellow-green and producing a very low source of yellow-green light at the ceiling, there is a decided sense of visibility in the room, even though it is darkened.

The floor of the laboratory is covered with heavy linoleum. The windows are fitted with steel frames in which heavy opaque shades may be raised or lowered in light tight compartments.

In concluding this paper, we desire to express our appreciation

to the firm of Carl Zeiss for their co-operation in the development of this apparatus. Our thanks, in particular, are due to Dr. W. G. Marquette of New York City and to Professor A. Kohler and Dr. J. Bauersfeld of Jena.

DISCUSSION

DR. F. M. WALTERS, JR.:[1] To discuss the paper by Mr. Lucas is like gilding the lily, but I am unable at this time to refrain from quoting that often-quoted saying that our advancements in science are due to 10 per cent inspiration and 90 per cent perspiration. Mr. Lucas' work, as well as that of other men in the scientific field, reflects the enormous care and attention which he has paid to details.

E. E. THUM:[2] I can, of course, only second what Dr. Walters has said about our high appreciation of Mr. Lucas's achievements in his avocation, as you might call it. He is one of those men who started out with a hobby and has been able to ride that hobby to the height of scientific achievement.

Apparently the people in England are more prone to do that than we are on this side. But I think we can match Mr. Lucas against some on the other side who have started out playing with something, as you might say, and who have been able to advance human welfare very materially with the results of their play.

It is very fine, indeed, that Mr. Lucas is connected with an organization that can appreciate the economic advantage of spending a large amount of money for the perfection and development of such a beautiful instrument as he has described. We can count on the fingers of a badly mutilated hand the number of commercial concerns in this country which would be willing to devote so much money to such a piece of advanced research equipment in the expectation of results, the economic significance of which cannot be listed in detail at the moment.

There is undoubtedly a great advantage in seeing things rather than inferring their existence. Some years ago Dr. Giolitti, the eminent Italian metallurgist, was discussing the results of X-ray investigations on the constitution of solid solutions which were just then being published. His attitude, while not exactly one of skepticism, was one where he repeatedly said, "I am not sure about this because I have not seen it."

Mr. Lucas's efforts to thrust back the border of the things that we can see further and further towards the minute things which we may infer by X-rays, are certainly to be praised. Obviously, the X-rays can show us only the *average* condition—something which will appear as a statistical result. From it we can get an idea of the average condition of a certain piece of metal, but when it comes to the actual distribution from one point to another of the particles which form this material, then we can only rely upon the visual sense, and naturally the further we can see down into the minute things, observable

[1]Carnegie Institute of Technology, Pittsburgh.

[2]Editor, *Metal Progress*, Cleveland.

at four or five thousand magnifications, the better information we will have about the ultimate structure of the things which we are studying.

Of course, that goes for other things besides metal, because Mr. Lucas has done invaluable work in other branches of science.

F. F. LUCAS: Many of my friends, including Mr. Thum, believe that I began the use of the microscope as a hobby. As a matter of fact, I have always regarded the microscope as a scientific tool for furthering professional research.

I wish to express a word of appreciation for the kind remarks of Dr. Walters and of Mr. Thum, even though I realize how little they are deserved.

I count it a privilege to have been invited to tell the members of the Society something about this new microscope.

LOW TEMPERATURE IMPACT STRENGTH OF SOME NORMALIZED LOW ALLOY STEELS

By John J. Egan, Walter Crafts, and A. B. Kinzel

Abstract

The authors have here presented the results of an investigation on the shock resistance of a number of low alloy steels in the normalized condition. Although —100 degrees Cent. might be considered as the lower limit at which any of these steels are applicable for engineering use, many possessed excellent properties at —80 degrees Cent. Among these are included chromium-copper, zirconium, Cromansil, nickel-vanadium, and nickel-copper steels. For use at temperatures below —100 degrees Cent. the higher alloy austenitic steels of the 18-8 type alone are suitable.

The combination of a deoxidizing or an austenite-forming element with a carbide former gives, in general, better low temperature properties than the combined decarbide and austenite-forming elements.

ADVANCES in chemical engineering and in transportation equipment have stressed the engineering importance of the low temperature properties of metals and alloys. It is scarcely necessary to mention specifically the improvements in the handling of liquefied gases, dewaxing of oils, and refrigeration, or the increased use of automobiles, aircraft and railroad equipment in climates where temperatures as low as —50 degrees Cent. are encountered. That the study of the properties of materials at low temperatures has great interest to metallurgists is obvious, and increasing efforts are being devoted to this field.

A perusal of the literature as well as common experience indicates definitely that the static properties of steels are not seriously altered at low temperatures. In general the ultimate strength and the yield point are increased, and the ductility decreased, the degree, however, being such as to cause no grave concern to the designing engineer. The impact strength, on the other hand, is generally low-

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. John J. Egan and Walter Crafts are research metallurgists, A. B. Kinzel is chief metallurgist, Union Carbide and Carbon Research Laboratories, Long Island City, N. Y. Manuscript received July 17, 1933.

ered to such an extent as to render many steels unsuitable for service under these conditions. It is the opinion of the authors that notched bar impact strength is a criterion of the ability of a metal to withstand deformation, not only in shock but in static two- or three-dimensional stress as well, and it is further an indication of the resistance of the material to notch fatigue. We have accordingly chosen to study only this property, which we consider one of the primary factors in determining the suitability of a steel for low temperature applications.

General experience as well as recorded studies, indicates very strongly that low temperature impact strength is improved by a quench and draw. However, the inability of satisfactorily quenching and drawing, either because of shape or size of the part, or both, makes steels in the normalized or as-rolled condition of greater interest to the engineer, so that the present investigation has been restricted to normalized steels. The austenitic steels have very high shock resistance even at very low temperatures, but their cost makes it more economical to use steels of lower alloy content in the intermediate low temperature range under consideration. For this reason only the low alloy steels were studied, and since it would be obviously impossible to consider every type, only those more common low alloy grades were chosen, as well as certain special analyses which for one reason or another were believed to have improved low temperature impact strength.

Steels Tested and Results

In order to establish a basis for comparison, plain carbon steels were first investigated, these steels as well as the standard S.A.E. alloy steels being obtained from standard commercial sources. Of the special steels studied some were made on a commercial scale and the remainder were produced in the small induction furnace at the Union Carbide and Carbon Research Laboratories. Chemical analyses together with the results of the impact tests in the three classes are shown in Tables I, II and III. Some of these values are shown in Table IV where they are arranged in the order of their tensile strengths.

Experimental Procedure

All tests were made on the standard 120 foot-pound capacity Izod machine using the 0.394 square inch (1 square centimeter) notched specimens, the notch angle being 45 degrees with a 0.026-

Table I
Low Temperature Properties of S.A.E. Steels

No.	Steel	S.A.E.	Impact Strength, Ft.-Lb. Per Sq.Cm. Room Temp.	−50° C.	−80° C.	−183° C.
1	C	1020	65.0	7.0	2.0	...
2	C	1030	49.0	9.0	5.0	...
3	C	1045	4.0	1.8	1.8	1.5
4	C	1050	11.0	5.0	3.5	1.0
5	C	1060	10.0	6.0	3.0	...
6	C	1080	2.5	2.0	...	...
7	C	1090	4.0	3.5	...	...
8	Ni	2335	15.0	8.0	5.5	2.0
9	Ni	2335	21.0	6.0	5.5	2.0
10	Ni-Cr	3135	15.0	7.0	4.0	2.3
11	Ni-Cr	3135	41.0	25.0	17.0	3.3
12	Ni-Cr	3140	17.0	9.0	7.0	2.5
13	Cr	5130	33.0	4.3	3.8	1.8
14	Cr-V	6120	21.0	6.0	4.8	1.5
15	Cr-V	6125	89.0	16.0	11.0	2.5
16	Cr-V	6135	24.0	14.0	6.0	2.0
17	Cr-V	6150	26.0	12.0	14.0	3.5

inch bottom radius, 0.079 inch deep. Values are reported as actually obtained, generally being quoted as foot-pound per square centimeter. No attempt has been made to convert these figures to foot-pound per square inch, as the authors do not feel that this is justifiable, since no definite general relationships had been shown to exist between impact strength and cross sectional area.

In all cases the specimens were cooled to the temperature in question in a liquid medium. Immersion for 30 minutes to 1 hour was followed by a quick transfer to the Izod vice with the immediate release of the hammer. Stop watch measurements showed that the complete operation could be carried out in from 3 to 4 seconds. Temperature loss during this interval was believed to be sufficiently slight as to be negligible, and the variation in temperature loss between specimens was naturally of a still lower order of magnitude. The liquid used varied with the temperature desired: viz., from 0 to —20 degrees Cent. ice water or iced brine; from —20 to —80 degrees Cent. acetone cooled with dry ice; from this point to —150 degrees Cent. liquid propane cooled by means of liquid air; and liquid air at —183 degrees Cent. The production of temperatures from —80 to —150 degrees Cent. was carried out with great care, the propane being placed in a Dewar flask, and a glass tube containing the liquid air immersed in it until the desired temperature was reached. At no time was any difficulty found in maintaining the temperature constant within limits of ±3 degrees Cent. Temperatures to —50 degrees Cent. were measured with a pentane thermometer. Below —50 degrees Cent. a suitably calibrated copper-constantan thermocouple and potentiometer were used.

Table II

Low Temperature Properties of Laboratory-Prepared Special Steels

No.	Steel	Analysis									Impact Strength, Ft.-Lb. Per Sq.Cm.				
		C	Mn	Si	Ni	Cr	Cu	V	Zr	Mo	Room Temp.	0°C.	−50°C.	−80°C.	−115°C.	−150°C.	−183°C.
20	Cr-Cu	.10	.24	.24	....	.83	.53	....	....	...	85	..	92	41.0	13.0	....	2.5
21	Mo	.13	.58	.24	....	....	....	....	....	.64	34	..	11	5.5	....	....	2.8
22	Ni-Cu	.14	.42	.18	2.26	....	1.00	....	....	...	71	..	35	22.0	17.0	10.0	3.0
23	Ni-V	.15	.32	.22	2.11	....	....	.57	....	...	75	..	19	17.0	15.0	4.0	3.0
24	V	.15	.35	.32	....	....	....	.46	....	...	76	..	29	14.0	3.0	2.0	3.0
25	Zr	.30	.33	.80	....	....	....	....	.15	...	34	25	10	5.0	2.0	2.0	2.0
26	Zr	.22	.35	.69	....	....	....	....	.26	...	76	54	20	15.0	3.0	2.0	1.5
27	Zr	.16	.37	.58	....	....	....	....	.66	...	87	..	71	34.0	3.0	2.5	2.5
28	Mn-Zr	.16	1.51	.60	....	....	....	....	.97	...	82	..	35	28.0	5.5	2.5	2.0
29	Cu-Zr	.19	.37	.84	....	....	1.08	....	.29	...	65	40	23	8.0	4.0	2.0	2.5
30	Ni-Zr	.21	.33	.67	2.85	....	....	....	.60	...	55	25	20	14.0	9.0	9.0	2.5
31	Mo-Zr	.16	.31	.67	....	....	....	....	.11	.64	35	..	12	7.0	....	....	2.0
32	Ni-Mo	.15	.52	.23	3.54	....	....	....	....	.39	40	..	13	8.0	5.0	5.0	3.0
33	Mn-Mo	.13	1.26	.18	....	....	....	....	....	.38	26	..	6	6.0	....	....	2.5
34	Mn-V	.17	1.54	.37	....	....	....	.54	....	...	38	..	15	14.0	1.5	1.5	4.0
35	Armco Iron									...	64	38	9	3.0	....	....	....

Table III

Low Temperature Properties of Commercially Prepared Special Steels

No.	Steel	Analysis									Impact Strength, Ft.-Lb. Per Sq.Cm.						
		C	Mn	Si	Ni	Cr	Cu	V	Zr	Mo	Room Temp.	0°C.	−50°C.	−80°C.	−115°C.	−150°C.	−183°C.
40	3% Cr	.25	.69	.25	....	2.89	....	....	....	...	18	..	12	9	....	....	3.5
41	Cromansil	.09	1.47	.55	....	.48	....	....	....	...	48	..	11	10	5.5	2.5	3.5
42	Zr	.07	.017	.35	....	....	....	....	.20	...	70	..	78	11	....	....	2.3

Table IV
Relation of Impact Strength to Tensile Strength of Steels Tested

No.	Steel	Ultimate Strength M. Lb.	Impact Strength, Ft.-Lb. Per Sq.Cm. Room Temp.	−50° C.	−80° C.
40	Rail	180–190	18.0	12.0	9.0
16	Cr-V	120–130	24.0	14.0	6.0
12	Ni-Cr	120–130	17.0	9.0	7.0
8	Ni	100–110	15.0	8.0	5.5
17	Cr-V	100–110	26.0	12.0	14.0
10	Ni-Cr	100–110	15.0	7.0	4.0
32	Ni-Mo	100–110	40.0	13.0	8.0
9	Ni	90–100	21.0	6.0	5.5
14	Cr-V	90–100	21.0	6.0	4.8
11	Ni-Cr	90–100	41.0	25.0	17.0
23	Ni-V	90–100	75.0	19.0	17.0
33	Mn-Mo	90–100	26.0	6.0	6.0
6	C	90–100	2.5	....	....
7	C	90–100	4.0	....	....
21	Mo	90–100	34.0	11.0	5.5
3	C	90–100	4.0	....	....
34	Mn-V	80–90	38.0	15.0	14.0
30	Ni-Zr	80–90	55.0	20.0	14.0
13	Cr	80–90	33.0	4.3	3.8
4	C	80–90	11.0	5.0	....
5	C	80–90	10.0	6.0	3.0
29	Cu-Zr	70–80	65.0	23.0	8.0
15	Cr-V	70–80	89.0	16.0	11.0
22	Ni-Cu	70–80	71.0	35.0	22.0
25	Zr	70–80	34.0	10.0	5.0
41	Cromansil	70–80	48.0	11.0	10.0
28	Mn-Zr	70–80	82.0	35.0	28.0
31	Mo-Zr	70–80	35.0	12.0	7.0
24	V	60–70	76.0	29.0	14.0
2	C	60–70	49.0	9.0	5.0
26	Zr	60–70	76.0	20.0	15.0
20	Cr-Cu	60–70	85.0	92.0	41.0
27	Zr	50–60	87.0	71.0	34.0
1	C	50–60	65.0	7.0	2.0
42	Zr	50–60	70.0	78.0	11.0
35	Armco Iron	40–50	64.0	9.0	3.0

In all cases specimens were machined to a one-half inch square bar and normalized from a suitable temperature. On air cooling they were placed vertically, transient air currents being avoided. Subsequently to normalizing the specimens were finish-machined to 0.394 inch square and notched by means of a fly cutter made to match a template against which the cutter was frequently checked to eliminate variations in the notch.

Discussion of Results

Typical impact strength-temperature curves may be seen in Fig. 1. The general tendency was for the impact value to fall rapidly to a low figure at some temperature between 0 and —100 degrees Cent. Between this temperature and —183 degrees Cent. little additional loss occurred, the impact resistance here being only 2-5 foot-pound. It would thus appear that in general the normalized

low alloy steels should not be used at temperatures below about —100 degrees Cent. for those engineering purposes where substantial impact strength is required. Steels for use in this range must be of the austenitic type. Fortunately, however, these temperatures are lower

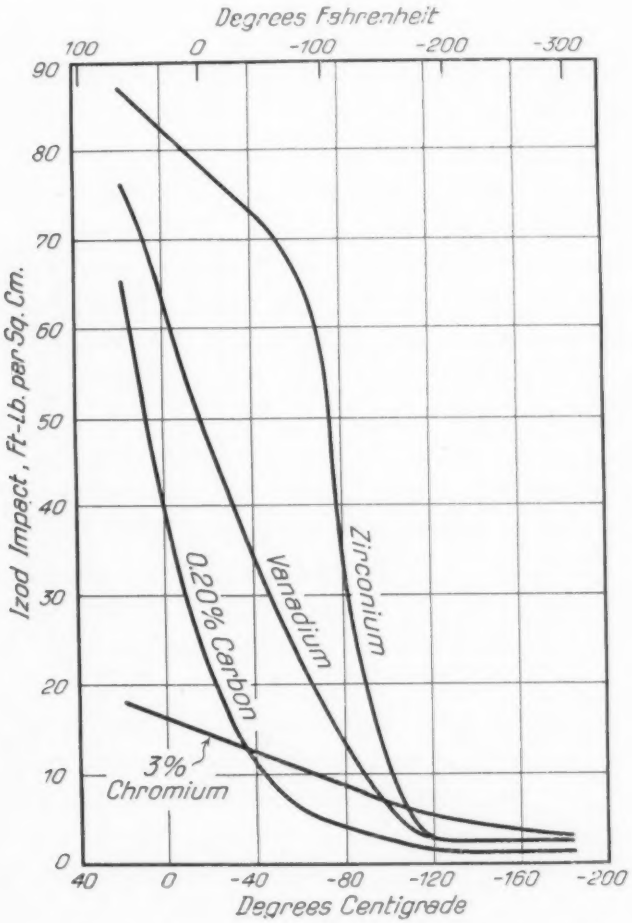


Fig. 1—Impact Strength of Typical Steels at Low Temperatures.

than are usually encountered, so that normalized pearlitic alloy steels are well adapted to most ordinary demands. The tests on these steels have therefore been made with special reference to temperatures in the range of —50 to —80 degrees Cent.

In addition to the poor values shown by the carbon and some of the alloy steels, a further disturbing factor was their erratic behavior. For example, the results of tests on chromium-nickel steels varied from 7 to 25 foot-pound at —50 degrees Cent. In another case known to the authors a normalized S.A.E. 2330 steel gave values

of 12 foot-pound even at liquid air temperature, whereas only 2 foot-pound were found on similar nickel steels in this study. The chromium-vanadium series also exhibited erratic properties. At —80 degrees Cent. a S.A.E. 6120 steel gave 5.5 foot-pound whereas a S.A.E. 6150 steel had an impact strength of 14 foot-pound. However, some of the steels, notably the zirconium series, were found to have relatively higher and more consistent impact strength.

Although certain alloy additions improved the impact resistance and reduced the inconsistencies, a survey of Table IV will show that steels having a tensile strength of less than about 80,000 pounds per square inch, had substantially less variation than those steels with higher strength. This condition may be compared with the similar lack of impact strength found in the usual normalized steels at normal atmospheric temperatures when a strength of 100,000 to 125,000 pounds per square inch is exceeded. It would therefore appear to be necessary to heat treat steels to obtain high tensile and impact strengths, but there are many uses where high shock resistance is not a primary requirement and normalized high strength steel should be suitable. For example, the average rail steel has an impact resistance of 2 foot-pound and is in general satisfactory except at very low temperatures. For this purpose then, the 3 per cent chromium steel in the air-cooled condition with 12 foot-pound at —50 degrees Cent. should be entirely safe for rail steel even though the strength is 180,000 pounds per square inch. Many other applications permit the use of steel with similar intermediate impact resistance, and it is evident that for such purposes a number of steels of the low alloy type that possess good static properties at high strengths would be suitable for use in the range of —50 to —80 degrees Cent.

The properties of many of the normalized low alloy steels were such as to render them quite satisfactory where a higher order of impact resistance would be required. This was not true of the plain carbon steels. Some alloys added little to the shock resistance of the carbon steels while others appeared to be effective only when two or more alloys were combined. These effects are brought out in Table V, which shows the relative influence of the alloy content, the degree being indicated by the number of plus or minus signs. Zirconium produced a decided improvement. Vanadium was very effective in raising the impact resistance, and improved results were also noted in steels containing chromium, molybdenum, nickel, copper, and manganese. The influence of zirconium and vanadium was found to in-

Table V

Relative Influence of Alloying Elements on Impact Strength at Low Temperatures

Effect of:	Relative Effect of Alloys −50° C.	−80° C.
Zirconium on Carbon Steel	+++	+++
Manganese on Zirconium Steel	0	0
Copper on Zirconium Steel	+	−
Nickel on Zirconium Steel	−	−
Molybdenum on Zirconium Steel	+	+
Vanadium on Carbon Steel	++	++
Manganese on Vanadium Steel	−−	−
Nickel on Vanadium Steel	−−	0
Chromium on Vanadium Steel	+	+
Chromium on Carbon Steel	+	+
Vanadium on Chromium Steel	+	+
Nickel on Chromium Steel	++	+
Manganese on Chromium Steel	+	+
Copper on Chromium Steel	+++	+++
Nickel on Carbon Steel	+	+
Chromium on Nickel Steel	+	+
Copper on Nickel Steel	+++	++
Zirconium on Nickel Steel	++	++
Vanadium on Nickel Steel	++	++
Molybdenum on Nickel Steel	+	+

crease in proportion to the alloy content, effective improvement being obtained at 0.50 to 1.00 per cent. In the case of the other alloys, however, no direct relation appeared to exist between alloy content and impovement, the effect being about the same irrespective of amount so long as an appreciable quantity was present.

Combinations of alloys produced rather surprising results. Zirconium steel was influenced only slightly by manganese and copper; it was harmed by nickel and improved by molybdenum. Vanadium steel was deleteriously affected by manganese and nickel and helped by chromium. Although nickel alone improved the normalized steel much less than might be expected from the reported results of heat treated specimens, additions of other alloys to nickel steel conferred a decided benefit. Chromium steel was improved by additions of vanadium, nickel, copper and manganese. The addition of zirconium and nickel improved molybdenum steels, while manganese had little effect. In classifying these results it was noted, in general, that the deoxidizing alloys, such as zirconium and vanadium, combined with the carbide-forming alloys chromium and molybdenum, gave good results, but that poor or doubtful results followed the combination of the austenite-forming nickel, copper, and manganese with the deoxidizing alloys zirconium and vanadium. Similarly, the carbide-forming alloys gave good results in combination with austenite-forming alloys. Although not strictly an exception, the nickel-vanadium steel gave good impact values. This may possibly have been

due to the intermediate position of vanadium between the deoxidizing and carbide-forming elements.

The above classification would indicate good properties in steels with the following alloy combinations:

Deoxidizing—Carbide	Austenite—Carbide
Zirconium	Nickel
Zirconium-Chromium	Nickel-Chromium
Vanadium	Copper
Vanadium-Chromium	Copper-Chromium

Typical results of the available steels in these classes, together with the nickel-vanadium and nickel-copper steels, which showed up particularly well, are shown in Table VI. With the exception of the nickel steel, all had very good impact strength even at —80 degrees Cent.

Summary

Although in general the low alloy normalized steels under the best conditions do not appear to be suitable for use in engineering application below —100 degrees Cent., many of them have sufficiently good impact resistance to make them suitable at —80 degrees Cent. If a limiting impact strength of 10 foot-pound be considered adequate, several steels in addition to those appearing in Table VI would be acceptable. Nickel-vanadium, nickel-copper, Cromansil, chromium-copper, zirconium, and vanadium would be satisfactory, while chromium-vanadium, manganese-vanadium, nickel, nickel-chromium, 3 per cent chromium, nickel-molybdenum, manganese-molybdenum, molybdenum, and plain carbon would be unsatisfactory. If we now consider the properties at —50 degrees Cent., which we have taken to be the limiting low temperature for service under atmospheric conditions, a slightly different listing en-

Table VI
Low Temperature Properties of Typical Steels of the Deoxidizing-Carbide and Austenite-Carbide Types

Heat	Steel	Impact Strength, Ft.-Lb. Per Sq.Cm. 20° C.	−50° C.	−80° C.
20	Chromium-Copper	85	92	41
27	Zirconium	87	71	34
24	Vanadium	76	29	14
9	Nickel	21	6	5.5
11	Nickel-Chromium	41	25	17
23	Nickel-Vanadium	75	19	17
22	Nickel-Copper	71	35	22

sues. All the steels listed at —80 degrees Cent. are of course also satisfactory at —50 degrees Cent. In addition 3 per cent chromium, chromium-vanadium, nickel-molybdenum, and plain molybdenum steels might be included. Carbon steels are in general not satisfactory below —15 degrees Cent. and may well be unsuitable at temperatures in the vicinity of 0 degrees Cent. depending upon their mode of manufacture.

In applications at —80 degrees Cent. when a higher order of impact strength is required, it would appear to be advisable to combine a deoxidizing or an austenite-forming element with a carbide-forming element. For such steels, zirconium and vanadium alone or suitably combined with other elements, or nickel, copper and chromium in combination as mentioned above have given the best results, the impact strengths varying from 14 to 41 foot-pound. At —50 degrees Cent. the values obtained on these steels are of the order of 20 to 35 foot-pound except for zirconium and chromium-copper steels, which were not impaired in impact strength at this temperature.

Conclusions

1. The common normalized low alloy steels of the types tested are not suitable for engineering applications below —100 degrees Cent.

2. Many normalized low alloy steels are suitable for engineering applications at temperatures down to —80 degrees Cent.

3. High impact resistance at temperatures down to —80 degrees Cent. may be obtained in low alloy normalized steels having a strength of less than about 80,000 pounds per square inch by combining a deoxidizing or austenite-forming element with a carbide-forming element.

4. Zirconium and vanadium markedly improve the low temperature impact strength of normalized low alloy steels.

5. When suitably combined with another alloy, chromium, nickel, copper, manganese and molybdenum improve the low temperature impact strength of normalized low alloy steels, the highest values being obtained with the chromium-copper combination.

Acknowledgment

The authors wish to express their appreciation of the interest and assistance given by the officers and members of the Union Car-

bide and Carbon Research Laboratories, Inc. Thanks are also due R. H. Dunlap for generous assistance in preparing and testing the material.

DISCUSSION

Written Discussion: By J. F. Cunningham, superintendent of testing laboratories, Civil Engineering Department, University of Manitoba, Winnipeg, Canada.

The authors are to be complimented on such a well thought out study of normalized or as-rolled shock resistance of alloy steels at low temperatures.

It has been found that intermediate and higher carbon steels in this condition are not dependable, but costs have often prohibited the use of them in "heat treated" conditions, while alloy steels have also been of questionable value.

The engineer can, from this paper, get a gleam of sunshine in learning that he may expect in the near future a steel with comparatively inexpensive alloys, which will stand up under some of the conditions he has to anticipate.

The minimum resistance to shock of most steels appears at or around —80 degrees Cent. which confirms the writer's experience.

The various transporatation methods in Canada are especially concerned with temperatures down to about —50 degrees Cent. Personal studies of data and experimental results would indicate a distinct brittle point somewhere between 0 and —50 degrees Cent. The majority of failures seem to occur at intermediate as well as extremely low climatic temperatures with a range between these two where failures are not so frequent.

The figures published for the 3 per cent chromium steel are very inviting and service tests of this steel under temperature conditions which have caused heavy casualties in carbon rail steels would be well worth while. The low carbon content of this steel is in its favor as the writer believes our present rail steel is too high in this element.

Rails in Russia have been reported good in wear and impact with a carbon content of less than 0.40 per cent carbon under similar climatic conditions to ours. The addition of chromium to low carbon may prove to give optimum toughness and abrasive qualities for rails if the price did not prove too high.

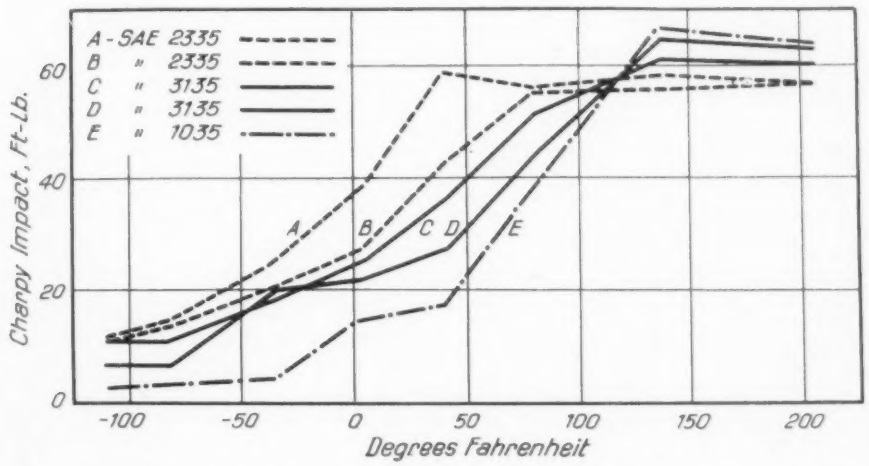
The subject of shock resistance at low atmospheric temperatures is coming into the limelight and many inexplicable failures of the past are being solved by efforts such as these authors bring forth.

Written Discussion: By N. B. Pilling, manager of research laboratory, International Nickel Co., New York City.

The main purpose of this paper, I would take it, is to discuss the tendencies which various alloying elements may have in preserving toughness in structural steels at subatmospheric temperatures, particularly after conditioning treatments of the simplest kind. The bulk of the data in support of this deal with steels of low carbon content, yet for purposes of comparison a number of the common S.A.E. steels of higher carbon content have been included. Few fine steels are ordinarily used in the simple normalized condition and as some doubt

might arise as to whether the useful low temperature impact properties which have been well established for several of the nickel steels in the heat treated condition* do persist under rougher conditions, it may be of interest to supplement the data in this paper with some recent Charpy impact results obtained by the International Nickel Co., in which three steels of similar carbon content are compared in the normalized condition; viz, S.A.E. 1035, 2335 and 3135.

It should be pointed out that in several respects these tests differ from those of Egan, Crafts and Kinzel. The steels were all from commercial pro-



Notched Bar Impact Tests on Normalized S.A.E. Steels.

duction, and include two random heats apiece of each alloy steel. All were normalized in 1 inch round sections instead of ½ inch square, and the standard Vee-notch with 0.01 inch radius which was used is appreciably sharper. The Charpy instrument has inherent advantages for low temperature testing, permitting as it does rapid and accurate placement of the specimen in register, coupled with a minimum of thermal disturbance in the notched region.

Inspection of these curves demonstrates that the familiar advantage of heat treated nickel steels over carbon steels is indeed maintained in the normalized condition to temperatures at least as low as —120 degrees Fahr.

The authors make an interesting comment regarding the erratic behavior of some common alloy steels in comparison with the new zirconium steels. Might it not be more accurate to say that the temperature range of transition from the normally tough, warm condition to the comparatively brittle, cold condition is so short that all steels show a considerable sensitivity, with regard to its precise location. Even the zirconium steels do not seem to be free from this habit as the data of Tables II and III show Izod values ranging from 10 to 78 at —60 degrees Fahr. (—50 degrees Cent.). While the curves shown above do not allow of course any very broad conclusion they do suggest that for these nickel and nickel-chromium steels at least we may reason-

*R. Sergeson, TRANSACTIONS, American Society for Steel Treating, Vol. XIX, No. 4, February, 1932.

ably expect them to show less variation in impact toughness at fairly low temperatures than may be found at normal temperatures.

Mark	S.A.E.	Chemical Analysis C	Mn	Si	P	S	Ni	Cr	Brinell Hardness
A	2335	0.35	0.62	0.21			3.30		179
B	2335	0.33	0.52		0.016	0.028	3.41		186
C	3135	0.38	0.50	0.17			1.18	0.58	185
D	3135	0.37	0.58	0.21			1.18	0.52	185
E	1035	0.35	0.68	0.20					142

O. W. Ellis: I have not had an opportunity of reading this paper, so that I am not clear whether the authors have specified exactly what they mean by normalized. In view of the fact that rates of cooling can have such pronounced influences on the microstructure of steel, and particularly upon such steels as contain chromium, I would be interested to know whether they have in any way correlated the results of their impact tests with the structures. I note in the list of test results that quite wide variations in impact values were obtained in the steels, 2335, 3135, and 6135, at temperatures of —50 and —80 degrees. Could the authors tell us whether those variations were obtained with steels that were structurally the same or whether they were obtained with steels which differed structurally as a result of variations in cooling rates?

R. A. Bull: I merely wanted to ask if any results were obtained on the copper-chromium steels, with the carbon content higher than 0.10 per cent.

J. J. Egan: The particular steel we investigated was 0.15 per cent carbon. That was the highest in that particular steel.

J. Fletcher Harper: I would like to ask the authors if they have made any tests on other materials which are commonly used for low temperature work, such as the austenitic type, and possibly the very high nickel type, which we could compare against these lower or possibly cheaper grades of steel. I am asking this question purely from an economic standpoint. We have used many of these higher grade steels, and possibly we could substitute the cheaper grades of material if we had a comparison based upon their technique.

A. V. deForest: I would also like to inquire whether these figures were also checked against unnotched specimens. It seems to me that in handing an engineer a notch-impact test figure he ought to realize at the same time that the results may be entirely misleading. His engineering structures should not contain notches anywhere, whether they are to be used at room temperature or at extremely low temperatures.

The presence of a sharp notch will lead to the development of a fatigue break under repeated stress, quite regardless of the impact notch properties which may be present in the metal. Very few pieces of engineering structure fail because of notch brittleness. The rail situation might be one to be discussed in that connection. When there are internal notches, the rail is a bad rail under any condition. If it has no notches it may be a perfectly good rail, regardless of whether its notch impact figure is exceedingly high or exceedingly low. I think we ought to know what constitutes a notch before we go to applying notch impact figures in engineering structures.

JEROME STRAUSS: I should like to refer to one matter that is rather close to the point which Mr. Pilling brought out at the end of his discussion, namely, the method of testing. Regardless of the short time interval between removal from the refrigerating unit and the actual testing, I am wondering what temperature change takes place at the surface of the notch of the test specimen, and to what extent this may be affected by the humidity in the room which influences the degree of formation of a frost film upon the specimen. This is extremely important in view of the major rôle played by the metal at the root of the notch in these impact tests. It is of interest that at least one laboratory in this country is equipped so that this question is of no importance, but unfortunately they cannot in an ordinary refrigerator conveniently reach liquid air temperatures.

Another point that I should like to bring out is that it is not satisfactory to compare steels made in the laboratory with commercial steels, first, because of the nature of the crystallization of the ingots, and second, because of the degree of reduction from ingot to test piece. This will be rendered clear by comparing one of the authors' steels with one that I have in mind at the moment, namely, the manganese-vanadium steel, which, in the authors' tests, normalized to a tensile strength of about 80,000 or 90,000 pounds per square inch, I wish to compare with another of very similar composition normalized to a tensile strength of 100,000 pounds per square inch. At room temperature the authors' steel shows an Izod value of 38, while the one to which I refer (commercial steel) showed a value in excess of 100. The authors give no intermediate value between −50 degrees Cent. and room temperature, so that absolute comparison is difficult but at an *actual* temperature of −41 degrees Fahr. the above commercial steel showed an Izod value of 30.5. The point is important in evaluating the data that are presented here.

One other matter that I should like to refer to is that we are working with two classes of engineering construction in considering these temperatures; the first, at from atmospheric temperature down to about −50 degrees Cent., and the other in chemical processes such as the liquefaction of gases, purification of helium and the like, in which the properties at −180 degrees Cent. approximately are of much importance. I have had occasion to mention previously, that it appears as though the low alloy steels behave very differently at these extremely low temperatures according to the nature of their heat treatment, and while the authors have considered only the normalized condition which alone is applicable to some forms of construction, I should like to refer to them the possibility of improving these rather brittle states by the consideration of other forms of heat treatment on these same steels.

Author's Closure

Regarding Major Bull's first question, we did not work on the chromium-copper steel with higher than 0.15 per cent carbon because these steels normalized at 65,000 pounds per square inch and while we hope that with further education the designing engineers will go to higher values we thought it best to stop at that point.

Mr. Ellis's comments are distinctly pertinent. We did not examine struc-

tures of these steels although we know that we would probably find differences in natural grain size, normality, and so on. We did, however, select the steels from varying sources not quite at random but from manufacturers who presumably were making steels satisfactory to the automotive industry. It was our purpose to see what the scatter would be under this set of conditions.

The accompanying table contains data on the 18-8 type of steel, in compliance with Mr. Harper's request. It might be said that down to about −50 degrees Cent. there is no deterioration in the shock resistance on the austenitic

Shock Resistance of 18-8

Temperature	Izod Value
Room	120.0 (machine capacity)
0° C.	120.0
−50	117.0
−80	113.0
Liquid Air	57.0

type of steels, and below that it drops off slowly. There is undoubtedly plenty of room for effecting economies by the use of these low alloy steels at temperatures down to −80 degrees Cent., and it is probably a question of the engineer's deciding for himself what the low limit is going to be. We have arbitrarily assumed 10 foot-pounds for purposes of discussion. Perhaps in some applications an engineer would rather have a higher minimum. Should it be 35 or 40, he would be restricted to the 18-8 type. If he feels that 10 foot-pounds would be satisfactory, in view of the fact that the ductility and the tensile strength are high, he can go to low alloy steels, as here shown.

Mr. deForest's comment regarding notch brings up one of our favorite subjects, as he well knows. In the course of this investigation we did not test any of the specimens unnotched, although we have done so in the past. In the unnotched specimens the values usually follow the run of the static figures. Naturally, we do not want notches in our engineering structures, and it has always been our point of view that we test notched bars not because we expect to have notches in our final structures but because engineering structures are subject to complex stresses. It is not a straight case of simple tensile stress. In almost all cases the stresses are at least two-dimensional, and often three-dimensional. The ductility of material in two- or three-dimensional stress is extremely different from that in single-dimensional stress. Theoretically, if there were any way to get balanced three-dimensional stress in tension, failure would take place with zero elongation in the most ductile material. We think that the notched impact test is a criterion of the ability of the material to distribute the two- and three-dimensional stresses, and have had some indication that this is so, not only on theoretical grounds but in practice as well.

With respect to Mr. Cunningham's discussion, the 3 per cent chromium steel for rails, which he notes particularly, has now been in service for about three years in Vermont (one location) where very low temperatures are experienced. During this period no troubles have been encountered. It is, therefore,

rather difficult to draw any extensive conclusions from this limited service. The other rails of this type have been in service under very heavy traffic conditions—high speed traffic conditions where temperatures as low as —30 degrees Cent. have been reached during the course of the last three years, and again no difficulties have been met with. Checking of the rails indicates no tendency toward transverse fissures or other phenomena. We naturally believe that this is an ideal rail steel because it seems to have all the desirable virtues.

Regarding the Russian experiment with 0.40 per cent carbon, there is not very much that we may learn from the European traffic conditions. The type of service is so very different from that which we have here and in Canada that it is quite possible that a 0.40 per cent carbon rail would show very little wear, whereas, in service here, it would fail in a very short time. While we agree that the trend should be toward lower carbon and higher alloy, it is our further belief that we are not justified in basing our conclusions on Russian experience.

Regarding Mr. Pilling's discussion, while there may be many applications at low temperatures for which the material is heat treated, our own experience has been to the contrary. In most of the low temperature work with which we have to deal, there was no opportunity for heat treatment because of the shape and nature of the piece. Moreover, we believe that particularly in low temperature work where the notch effect is so dangerous, safety would indicate that a drastic quench be omitted and that normalizing steels be used. Mr. Pilling's work fails to give the values from which the curves were drawn and we are left to assume that they pass through all points. Neither does he mention the number of tests made between room temperature and —125 degrees Cent. Our work has shown that certain steels behave rather erratically in shock at low temperatures and we fail to see that four steels, as quoted by Mr. Pilling, should in any way disprove it.

In our opinion the never-ending discussion as to the comparative virtues of the Izod and the Charpy machines is largely academic. What we want is something that will give us a relative order of magnitude—whether it is 2 or 3 per cent one way or another makes little difference. A few degrees difference in temperature, even when the curves are fairly steep, does not account for the difference in order of magnitude found among the steels themselves, and while there may be a change in temperature in the specimens when put in the Izod, the difference between various specimens is certainly of a second order of magnitude. All specimens become covered with frost very quickly after removal from the cooling medium and as this frost no doubt acts as an insulating layer slight differences in time thereafter have very little effect. The zirconium steel does show a rather steep drop in impact with temperature, as pointed out by Mr. Pilling, but that drop, which is so steep, occurs only after —50 degrees Cent. has been passed. In other words, in the useful atmospheric range the drop is very small.

Referring again to our reasons for choosing the normalizing treatment, although there are other methods of heat treatment there are certainly none as simple and as readily applicable as normalizing, particularly if we stop thinking about atmospheric work and come to some of the larger pressure vessels that are being used in connection with certain types of oxygen installation, the de-

waxing process, and certain of the chemical industries. To quench these or treat them in any drastic way would be actually hazardous.

One other point that was brought up is the difference between the laboratory steels and the commercial steels. We are very fully aware of that, and because of it have purposely listed the laboratory steels and commercial steels in two separate tables. There is one thing about the laboratory steels that has been confirmed by Mr. Strauss's comments. To the best of our knowledge we have never as yet had a laboratory-made steel that did not show poorer properties than were obtained with the commercial steels later on.

The manganese-vanadium steels were also tested and are among the very best in the group, but as Mr. Egan pointed out, the chromium-coppers stand out very markedly above all of the others.

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Vol. XXI No. 12
December, 1933

The TRANSACTIONS *of the* AMERICAN SOCIETY *for* STEEL TREATING

Published monthly and Copyrighted, 1933, by the AMERICAN SOCIETY FOR STEEL TREATING, *7016 Euclid Avenue, Cleveland, Ohio*

SUBSCRIPTIONS: (members) $2.50 per year
(non-members) $5.00 per year, $1.00 per copy
Foreign (non-members) $6.50 per year, $1.25 per copy

Entered as second class matter, November 9, 1931, at the Post Office at Cleveland, Ohio, under the Act of March 3, 1879.

RAY T. BAYLESS, *Editor*

Vol. XXI December, 1933 No. 12

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